Introduction to fuel cells: Fundamentals of electrochemical kinetics, thermodynamics and solid state chemistry for the experienced (II)

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Introduction to fuel cells: Fundamentals of electrochemical kinetics, thermodynamics and solid state chemistry (II) for the experienced

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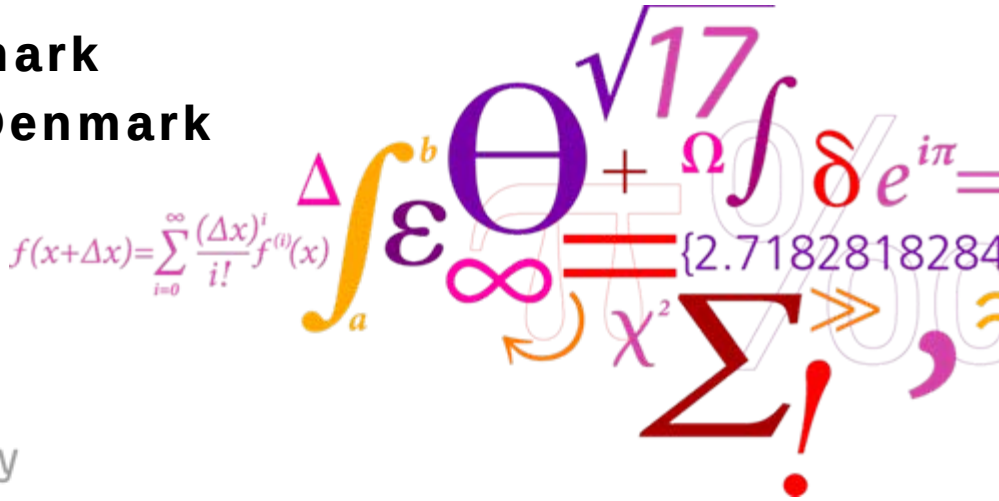

Risø DTU
National Laboratory for Sustainable Energy

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- Potential concepts - energy and voltage
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- Measurements of electrolyte resistance, reaction resistance and electrode overvoltage by EIS
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Basics

A fuel cell is a galvanic cell also called an electrochemical cell

The relation between the chemical energy, ΔG (Gibbs free energy of reaction) of a cell reaction and the equilibrium (ideal) electrical voltage, also called the electromotive force, Emf, of the cell is given by

$$-\Delta G = n \cdot F \cdot Emf$$

n is the number of electrons exchanged in the total reaction, and F is The Faraday constant = 96485 As/mol

Basics

Important: ΔG and n must refer to the same reaction scheme!

Example 1:

$$H_2 + O^{2-} \leftrightarrows H_2O + 2e^-$$
$$\underline{\tfrac{1}{2}O_2 + 2e^- \leftrightarrows O^{2-}}$$
$$H_2 + \tfrac{1}{2}O_2 \leftrightarrows H_2O$$

$n = 2$ and $\Delta G^0_{298} = -286$ kJ/mol H_2

Example 2:

$$2H_2 + 2O^{2-} \leftrightarrows 2H_2O + 4e^-$$
$$\underline{O_2 + 4e^- \leftrightarrows 2O^{2-}}$$
$$2H_2 + O_2 \leftrightarrows 2H_2O$$

$n = 4$ and $\Delta G^0_{298} = -572$ kJ/mol O_2

Basics

At standard conditions (25 °C and 1 atm):

Emf = $-\Delta G^0/(nF)$ =
$-(-286\ kJ/mol)/(2*96485\ As/mol)$ =
$-(-572\ kJ/mol)/(4*96485\ As/mol) = 1.23\ V$

$\Delta G = \Delta G^0 + RT\ln K$, K is the constant in the law of mass action

This gives us the Nernst equation:

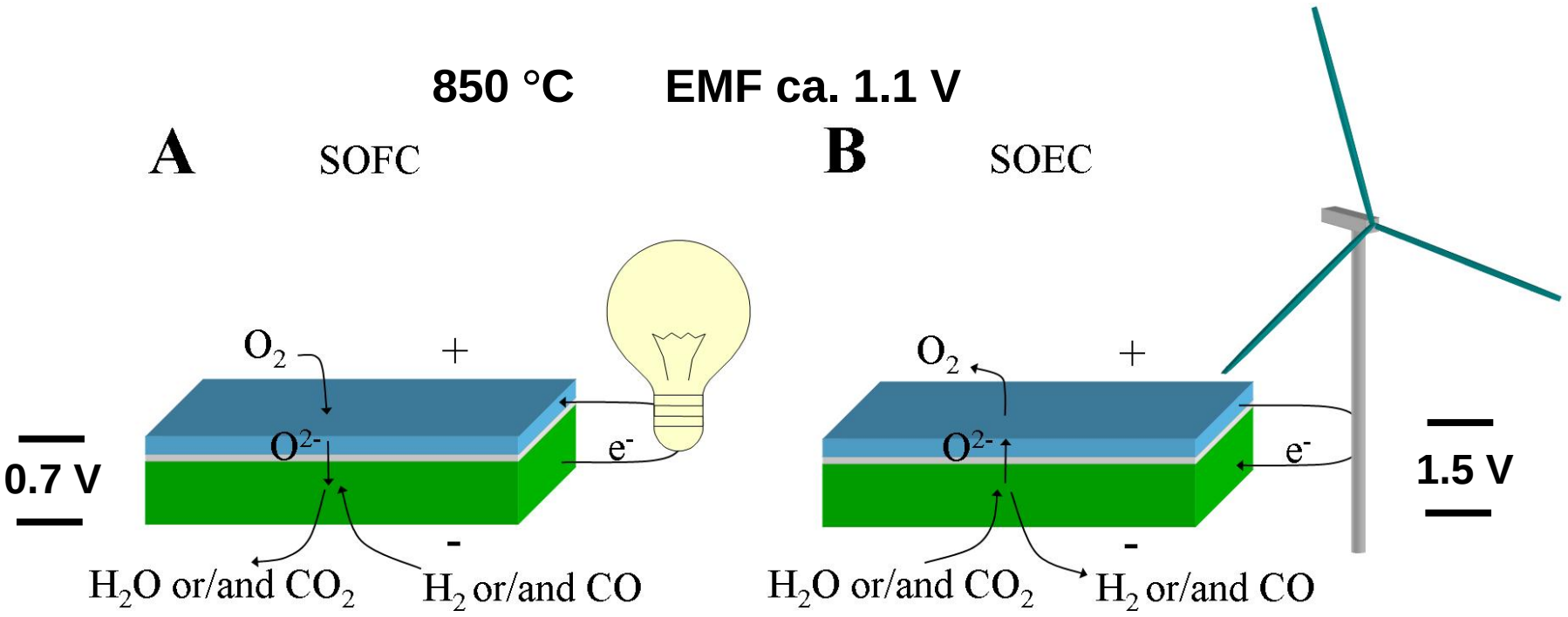
$$E = E_0 + \frac{RT}{nF} \ln \frac{P_{H_2O}}{P_{H_2} \sqrt{P_{O_2}}}$$

Basics

The cell voltage may deviate from the theoretical Nernst voltage. Some possible reasons are

1. **The cell is under external electrical load**
2. **The cell has an internal electronic leak**
3. **The concentration of reactants are different from the assumed values e.g. due to gas leakage**
4. **The actual cell temperature is different from the measured**
5. **The cell has a thermal gradient, i.e. the Emf + a thermoelectric voltage is measured**

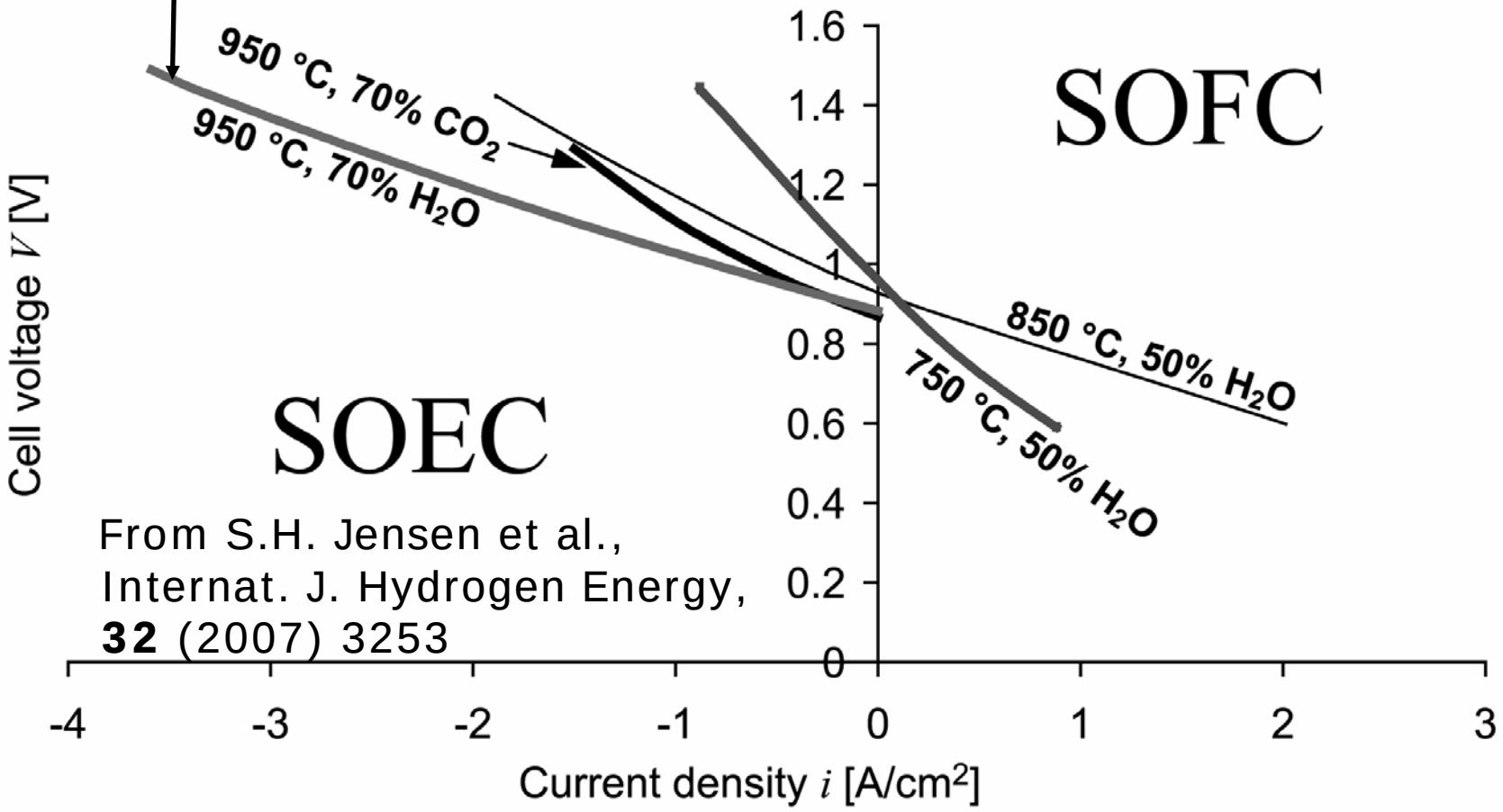
The reversible SOC



Working principle of a reversible Solid Oxide Cell (SOC). The cell can be operated as a SOFC (A) and as a SOEC (B).

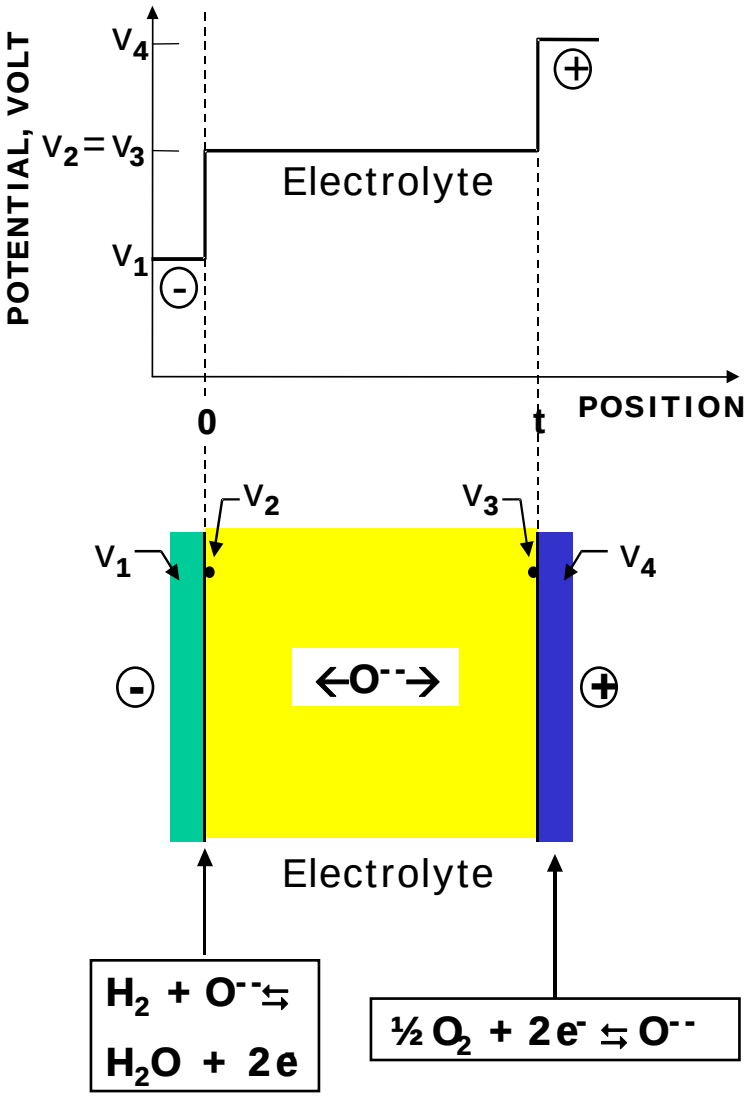
Reversible SOC

World record in electrolysis



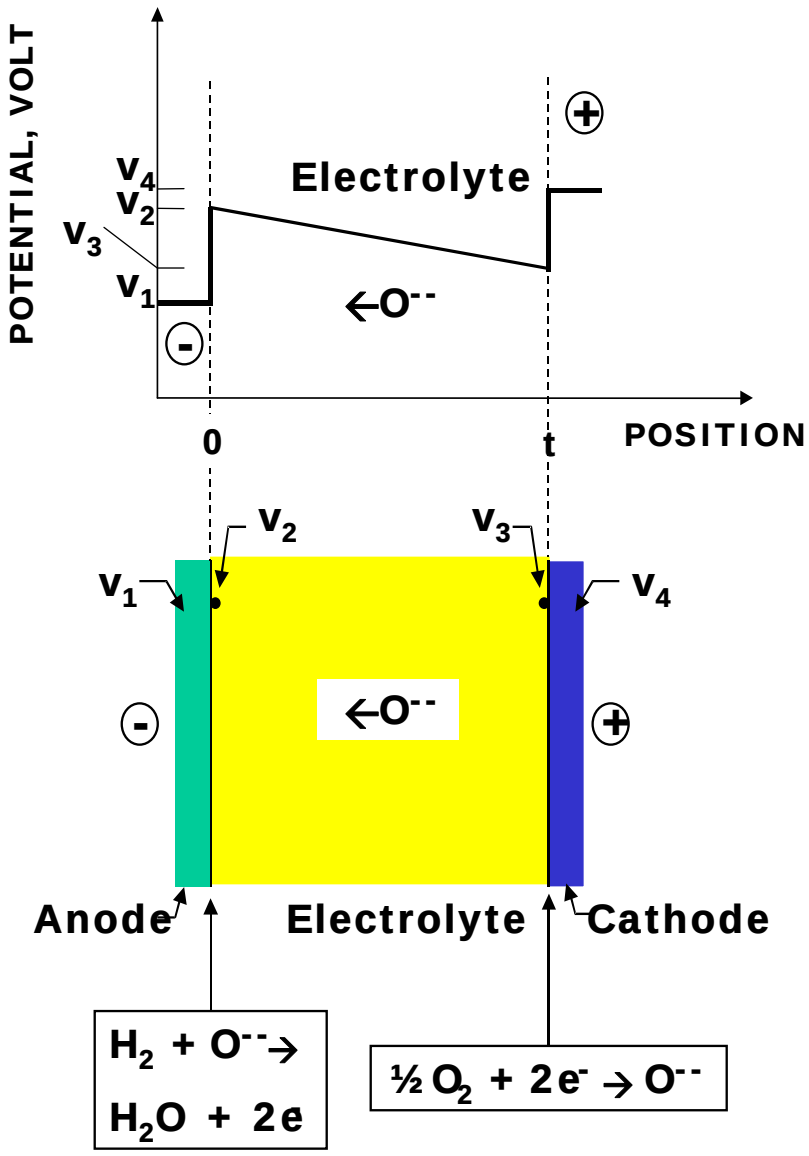
From S.H. Jensen et al., Internat. J. Hydrogen Energy, **32** (2007) 3253

Potential through the electrode supported cell with no current - simplified



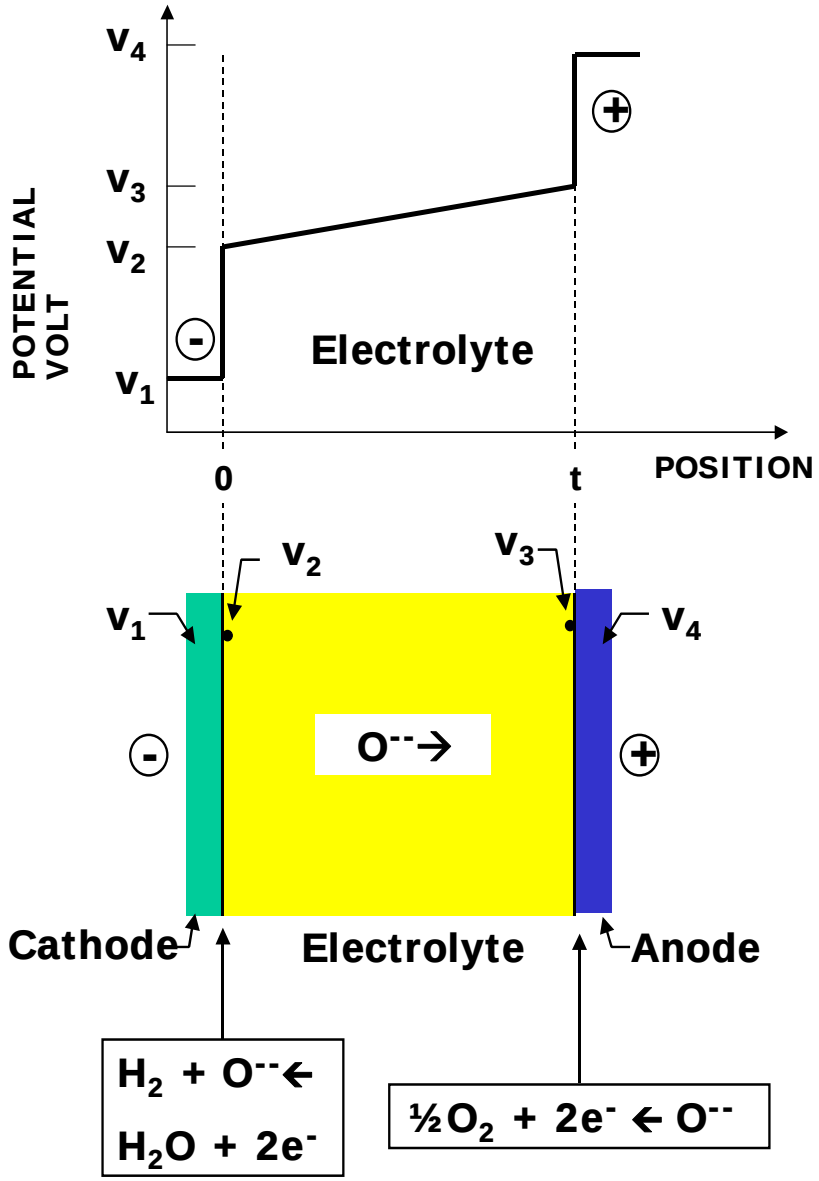
$V_4 - V_1 = Emf$

$Emf = -\Delta G / (n \cdot F)$



Potential through a cell with a current load in fuel cell mode - simplified

Cell voltage smaller than Emf



Potential through a cell with a current load in electrolyser cell mode - simplified

Cell voltage larger than Emf

Potential concepts - energy and voltage

The electrochemical potential of an electron is defined as

$$\overline{\mu}_{e^-} = \mu_{e^-} - F\phi$$

where μ_{e^-} is the chemical potential of the electron, F is Faradays number, and ϕ is the electrical potential inside the material in which the electron is. ϕ is called the Galvani potential, the inner potential or the electrostatic potential. It is no possible to measure the absolute value of ϕ, but we can by measurement determine the difference in Galvani potential of two planes in a material if the material is homogeneous.

The electrochemical and the chemical potential are both specific energy quantities, J/mol, whereas the Galvani potential has the unit of voltage, V.

Potential concepts - energy and voltage (cont.)

What we can measure with a voltmeter is the electromotive potential, π, defined as

$$\pi = -\overline{\mu}_{e^-} / F$$

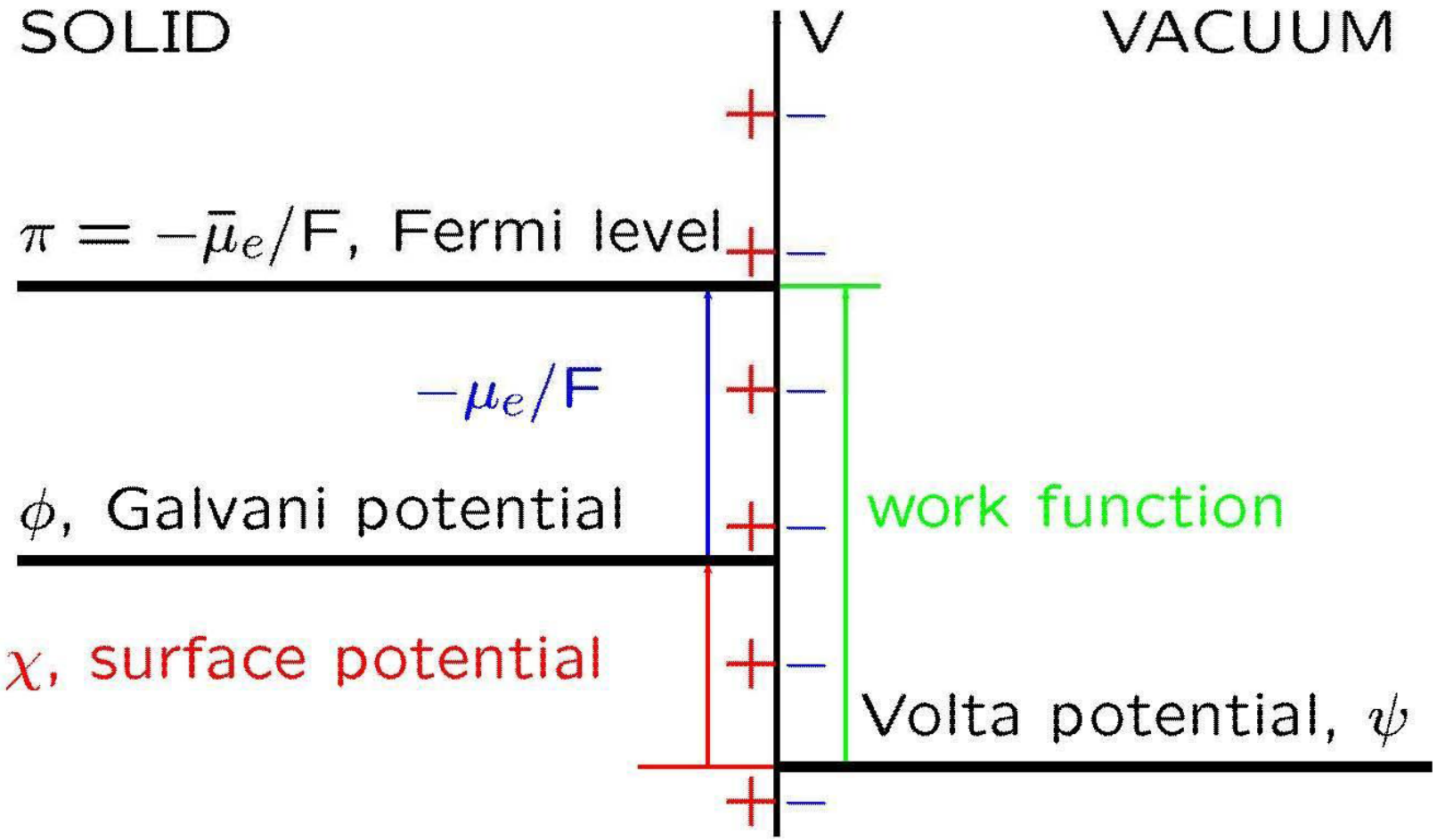
This means that the electromotive potential is dependent on both the concentration of electrons and the Galvani potential

$$\pi = -\overline{\mu}_{e^-} / F = (-\mu^{\ominus}_{e^-} - RT \ln(c_{e^-} / c^{\ominus}_{e^-})) / F + \phi$$

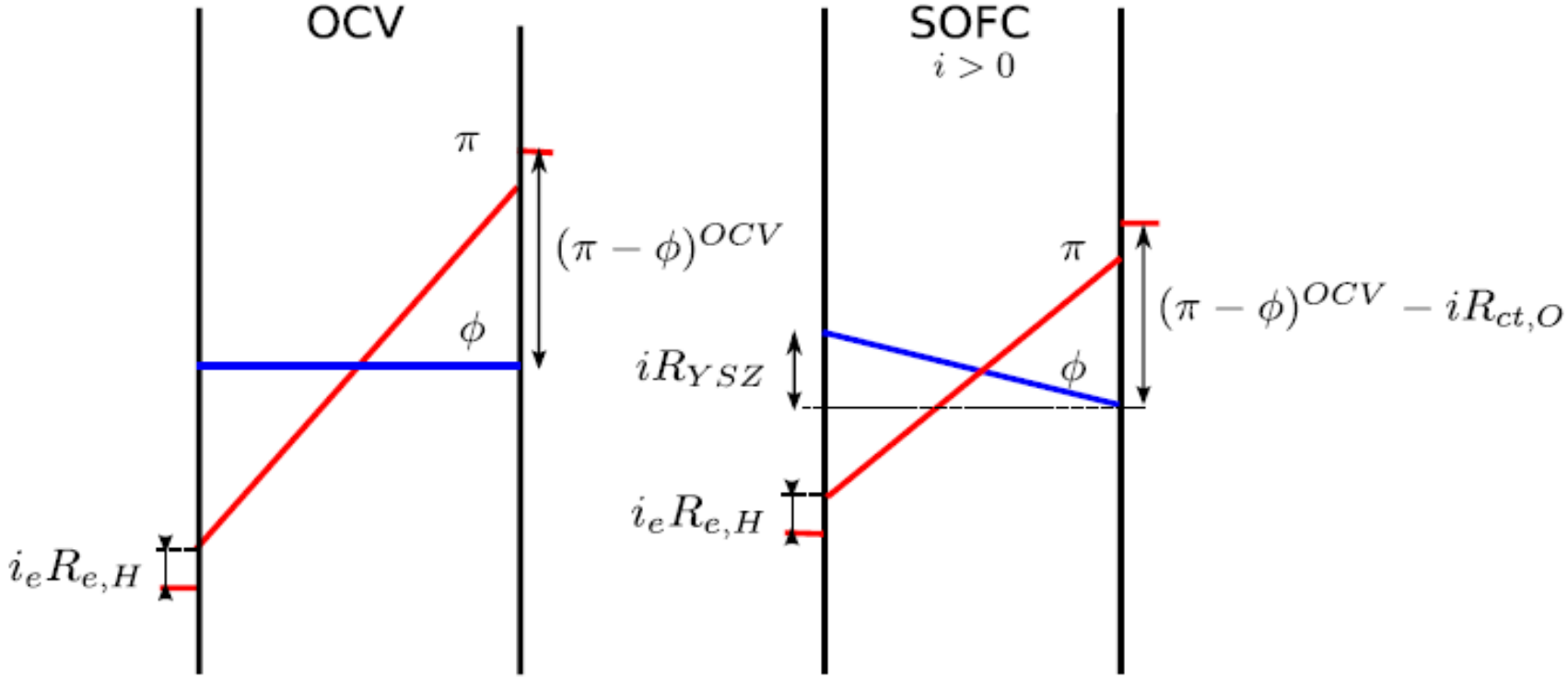
where $\mu^{\ominus}_{e^-}$ is the standard state (or reference) concentration of the electrons

Let us look at a picture of the general potential concepts and afterwards see what this may be used for in practise.

The electric potentials in more details

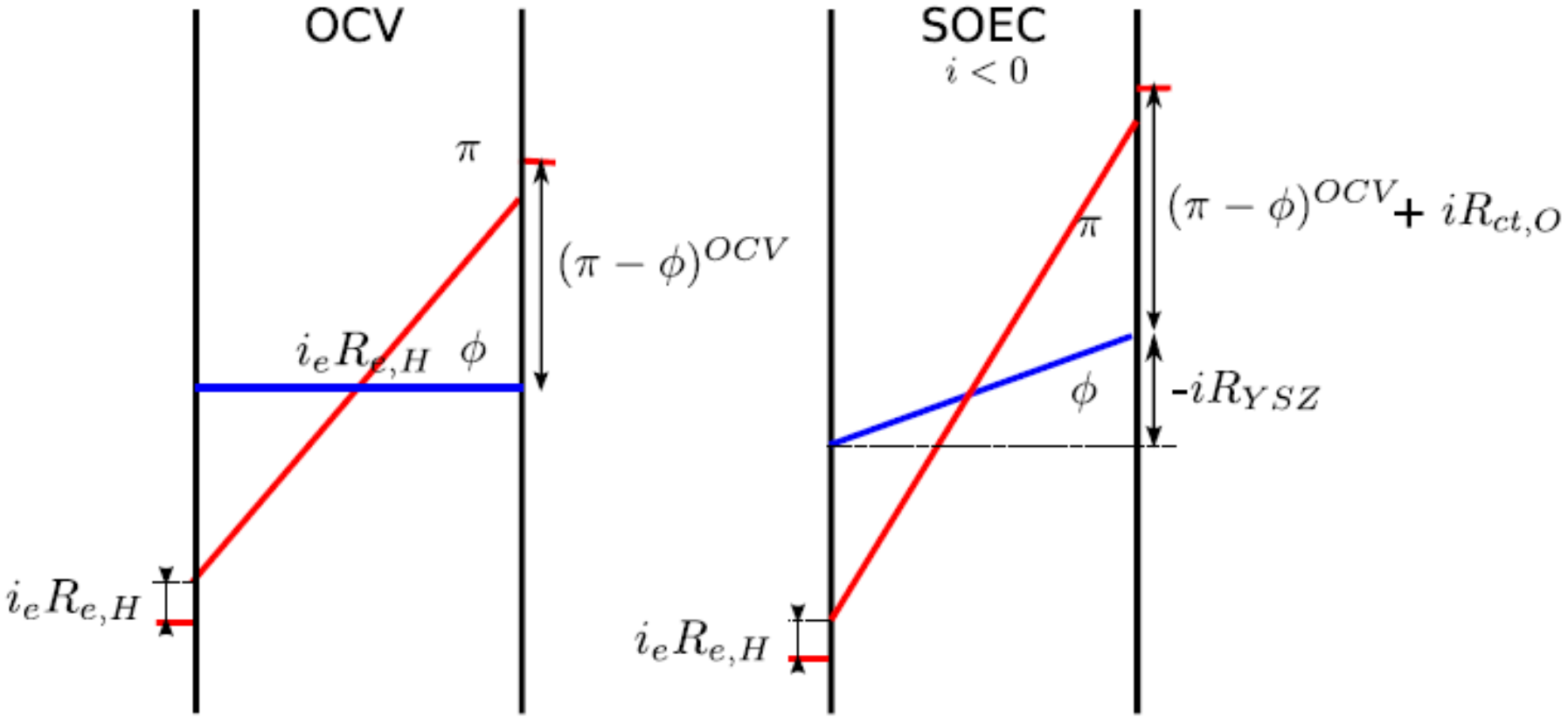


The electric potentials in more details (cont.)



Sketch of profiles for the electromotive potential, π, and the Galvani potential, ϕ, in a solid oxide fuel cell. The oxygen electrode is to the right. The absolute positions of the potentials are arbitrarily chosen.

The electric potentials in more details (cont.)



Sketch of profiles for the electromotive potential, π, and the Galvani potential, ϕ in a solid oxide electrolyser cell. The oxygen electrode is to the right. The absolute positions of the potentials are arbitrarily chosen.

Examples of a YSZ based cell

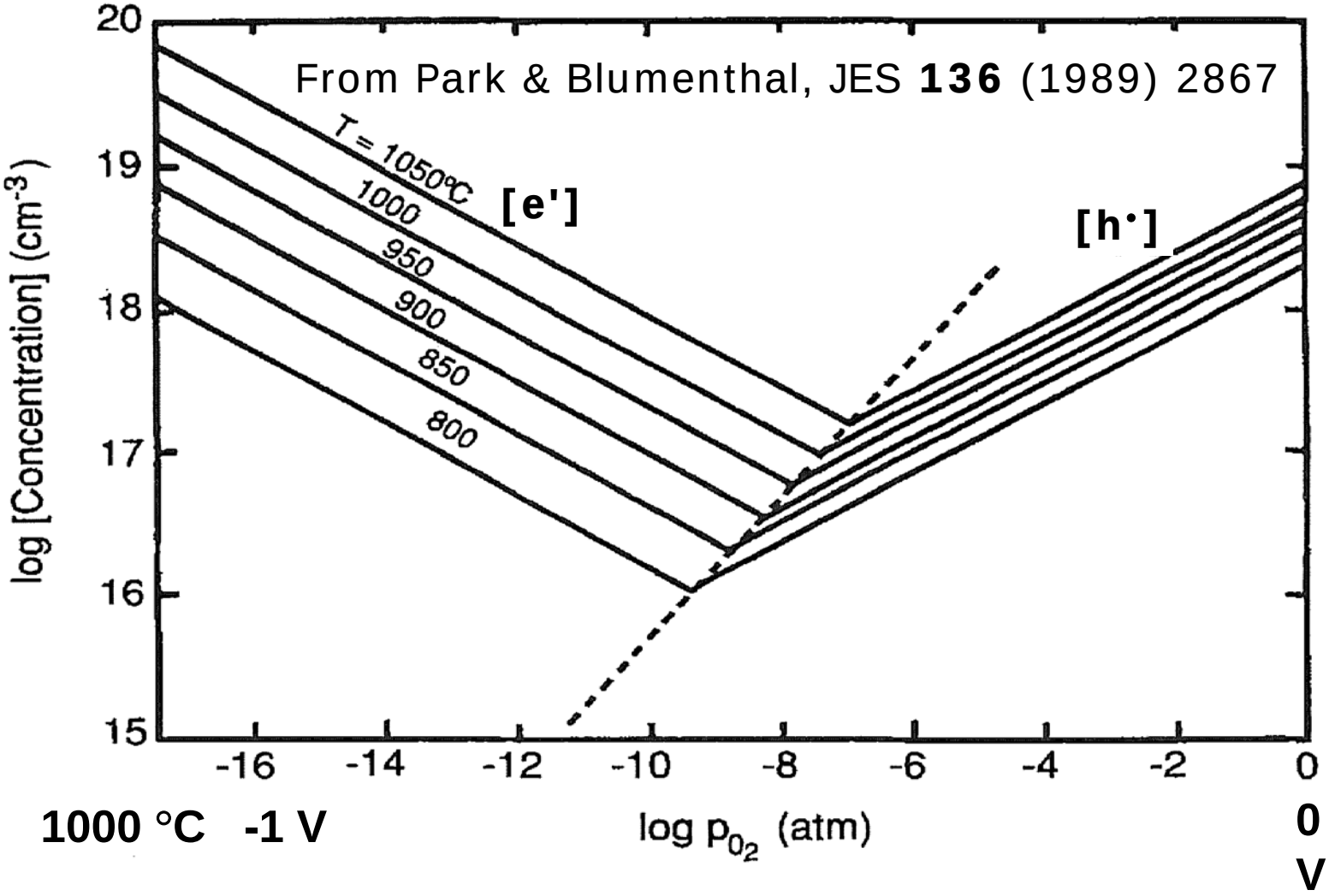
The following results are from: T. Jacobsen and M. Mogensen, ECS Transactions, 13 (26) (2008) 259-273

Transport and concentration data for 8 mol% YSZ from J. H. Park and R.N. Blumenthal, J. Electrochem. Soc., 136 (1989) 2867

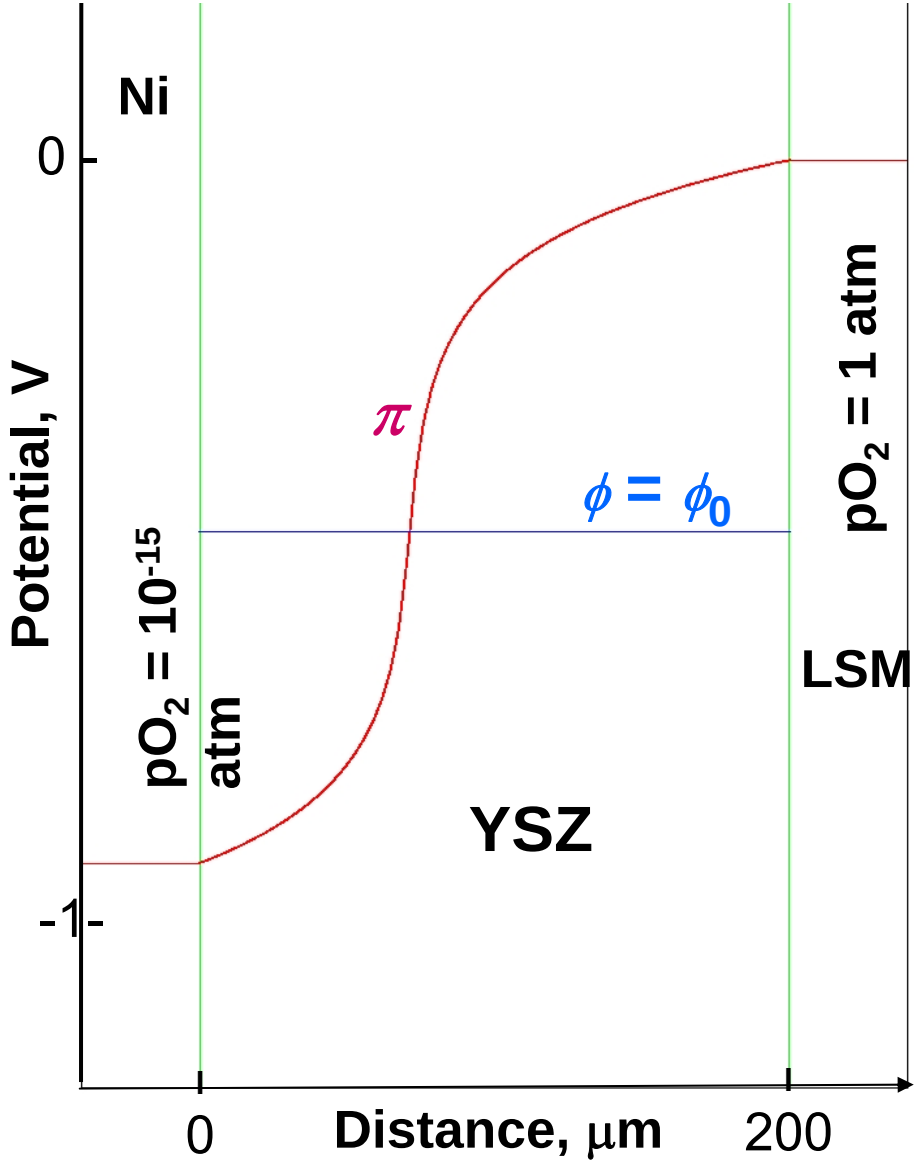
Further data used in calculations given below (not from experiments):

Electrode thickness	**L = 200 μm**
Temperature	**T = 1000 °C**
Oxygen pressure, right	**pO_2 = 0.2 bar**
Oxygen pressure, left	**$pO_2 = 1.00 \cdot 10^{-15}$ bar**
SOFC current	**$i = 1.00 A\ cm^{-2}$**
SOEC current	**$i = -1.00 A\ cm^{-2}$**
Charge transfer resistances:	
$H_2 + O^{2-} \leftrightarrows H_2O + 2e^-$	**$R_{ct,H} = 0.05\ ohm\ cm^2$**
$½\ O_2 + 2e^- \leftrightarrows 2O^{2-}$	**$R_{ct,O} = 0.1\ ohm cm^2$**
Electron transfer	**$R_{e,H} = 0.01\ ohm\ cm^2$**
Electron transfer	**$R_{e,O} = 0.01\ ohm\ cm^2$**

Electron defect concentration in YSZ



Potential course, OCV, 1000 °C



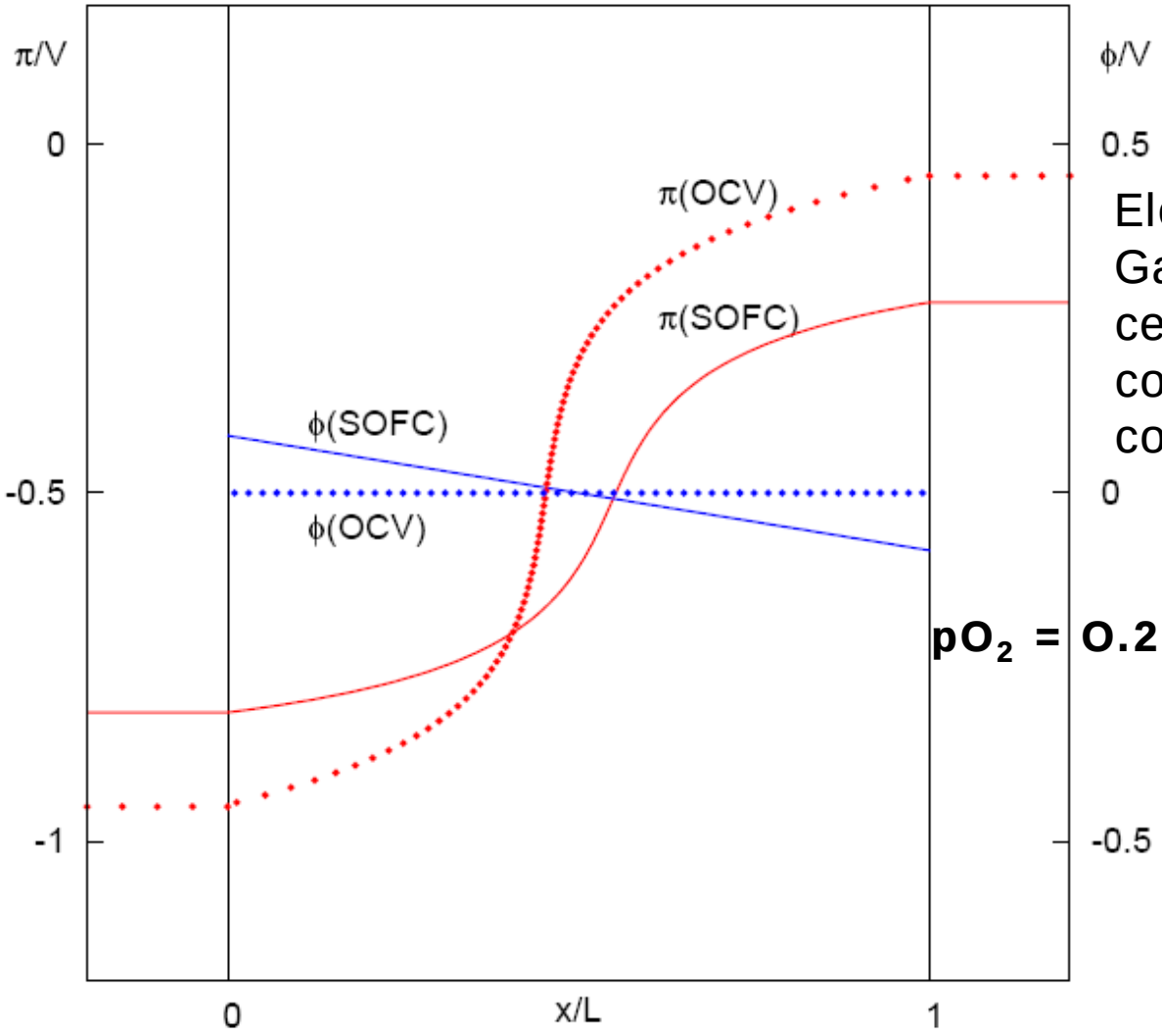
$$\pi - \phi + \phi_0 = \frac{RT}{4F}\ln(pO_2)$$

where ϕ_0 is the Galvani potential at zero current. If we define ϕ_0 as zero, then

$$\pi - \phi = \frac{RT}{4F}\ln(pO_2)$$

Thus, from this equation the local pO2 **may be calculated**

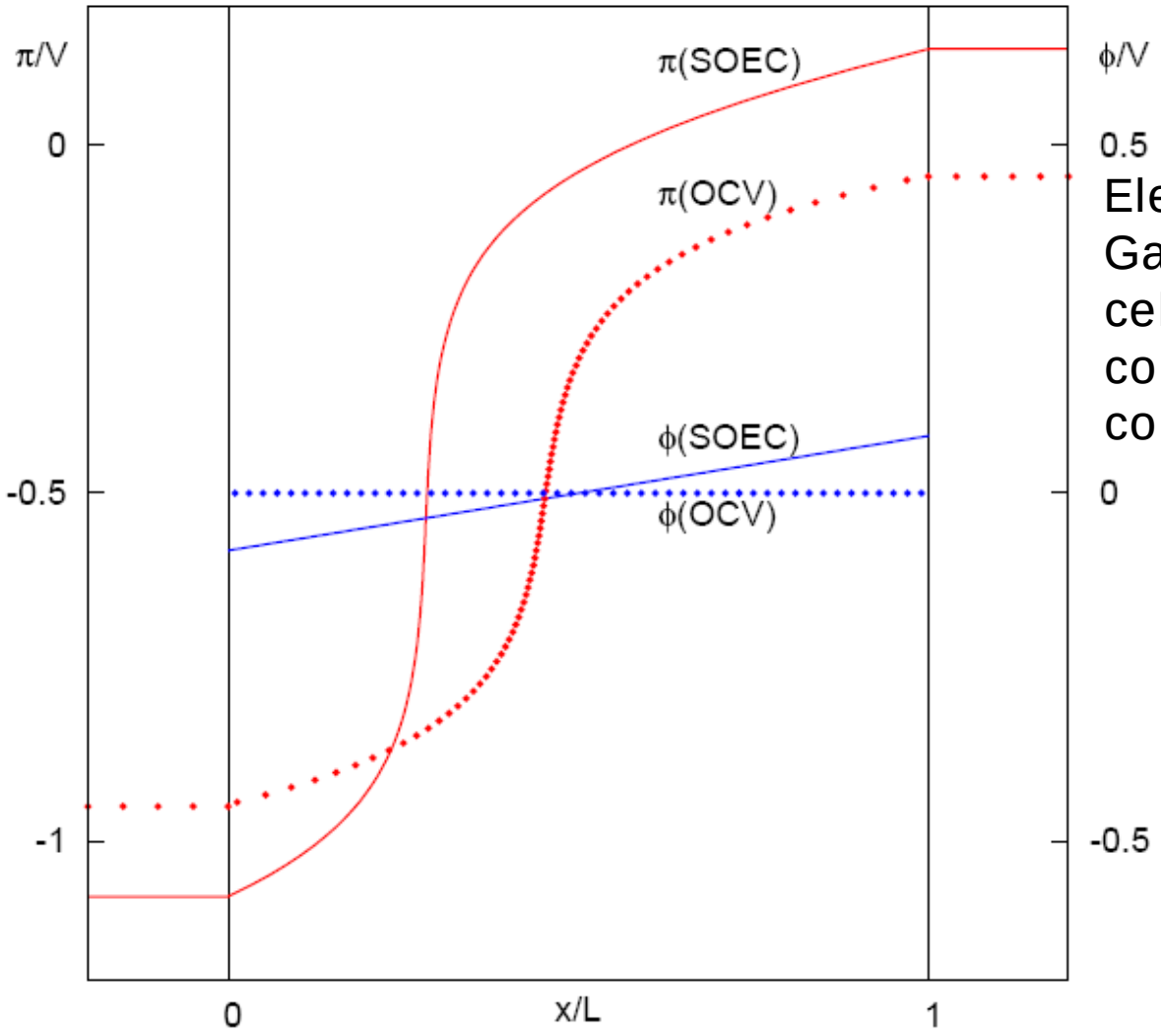
Potential course, SOFC mode



Electromotive, π, and Galvani, ϕ, potentials in a cell operating in SOFC mode compared to open circuit conditions at 1000 °C.

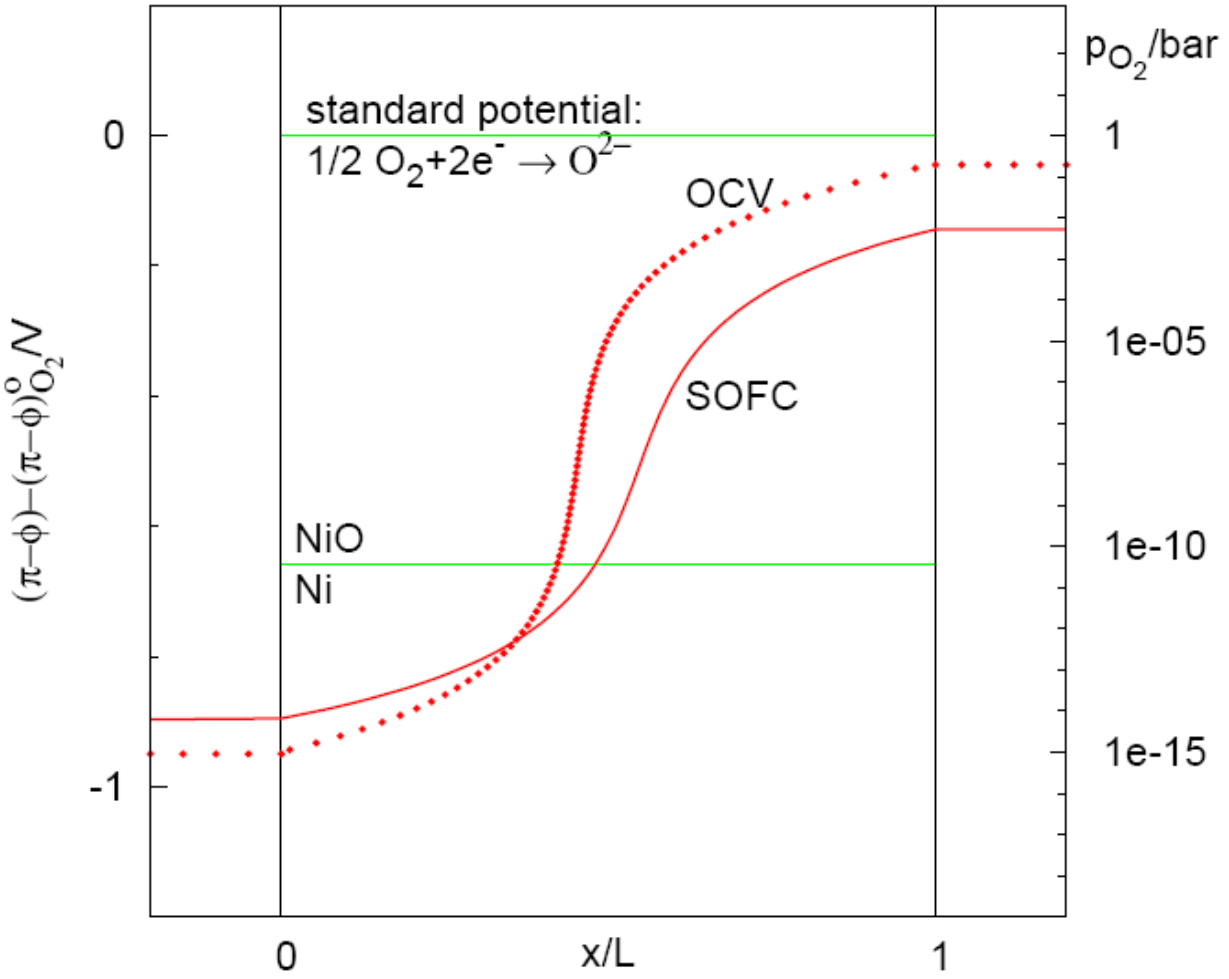
pO_2 = O.2 bar

Potential course, SOEC mode



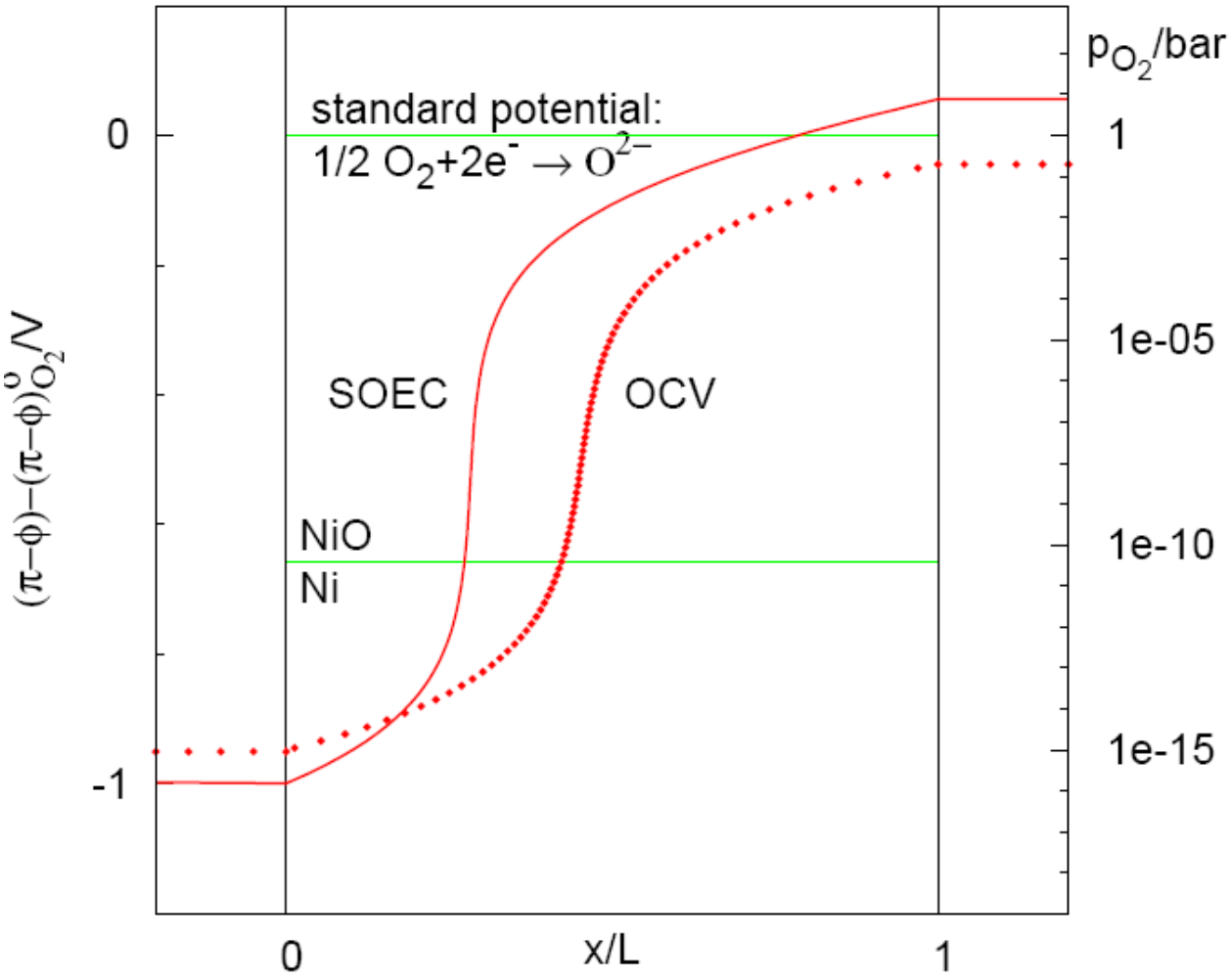
Electromotive, π, and Galvani, ϕ, potentials in a cell operating in SOFC mode compared to open circuit conditions at 1000 °C.

Course of oxygen partial pressure SOFC mode



π-ϕ and local equilibrium oxygen pressure in a cell operating in SOFC mode compared to open circuit conditions at 1000 °C

Course of oxygen partial pressure SOEC mode



π-ϕ and local equilibrium oxygen pressure in a cell operating in SOEC mode compared to open circuit conditions at 1000 °C

Conclusion on potentials

- **Several types of concepts of potential exist**
- **The driving force for the electrons of very low concentration in a good solid electrolyte, is the electromotive potential, which is mainly reflecting the concentrations of electrons, n, and holes, h.**
- **The driving force for oxide vacancies or interstitial protons of high constant concentration, is the Galvani (also called electrostatic) potential gradient, which is formed by the chemical driving forces of the electrode reactions.**

Questions 1

- **My question to you:**
- **Is the cell voltage of an electrolysis cell higher than the cell voltage of a fuel cell in case that the gas composition at the electrodes is the same?**

Polarisation of a cell

- When current is drawn form a fuel cell the voltage decrease below the Emf, the bigger drop, the higher the current density.
- This voltage drop is often referred to as cell polarisation.
- The part of the polarisation that is due to the sluggishness of the electrode reaction is called activation overvoltage (or overpotential) and the overvoltage due to changes in the reactant concentrations is called concentration overvoltage.
- The voltage drops due to the resistance of the electrolyte and due to non-ideal contacts are not overvoltges but just polarisations.
- Everything is just with opposite sign in case of electrolysis.

Types of polarisation resistance

The area specific resistance, ASR, may be broken down into five contributing area specific polarisation resistances:

$$ASR = R_{elyt} + R_{connect} + R_{p;elchem} + R_{p;diff} + R_{p;conver}$$

The ohmic polarisation, ΔU_{elyt}, is due to the electrolyte resistance and follows Ohm's law:

$$\Delta U_{elyt} = R_{elyt} \cdot i \qquad [\Omega\ cm^2 \cdot A\ cm^{-2} = V]$$

Contact resistance

Contact resistance may often be equal to constriction resistance (e.g. current collectors in the cell test set-up) , because:

- **Two bodies in contact (without pressure) will touch each other in 3 points.**
- **If the bodies are made of hard materials the contacts areas are almost only contact points.**
- **Thus the current path is constricted to go through these small contact areas.**

Literature: R. Holm, Electrical contacts, Theory and Applications, 4. edition, printed in 2000, Springer, Berlin

Small electrical contacts

α is the radius of a circular contact

$\mu$is a parameter, and the distance along the y-axis is y = sqrt(μ)

Total resistance R = $1/(4\alpha\sigma)$

5/6R:; 3.7 α

From: R. Holm, Electrical contacts

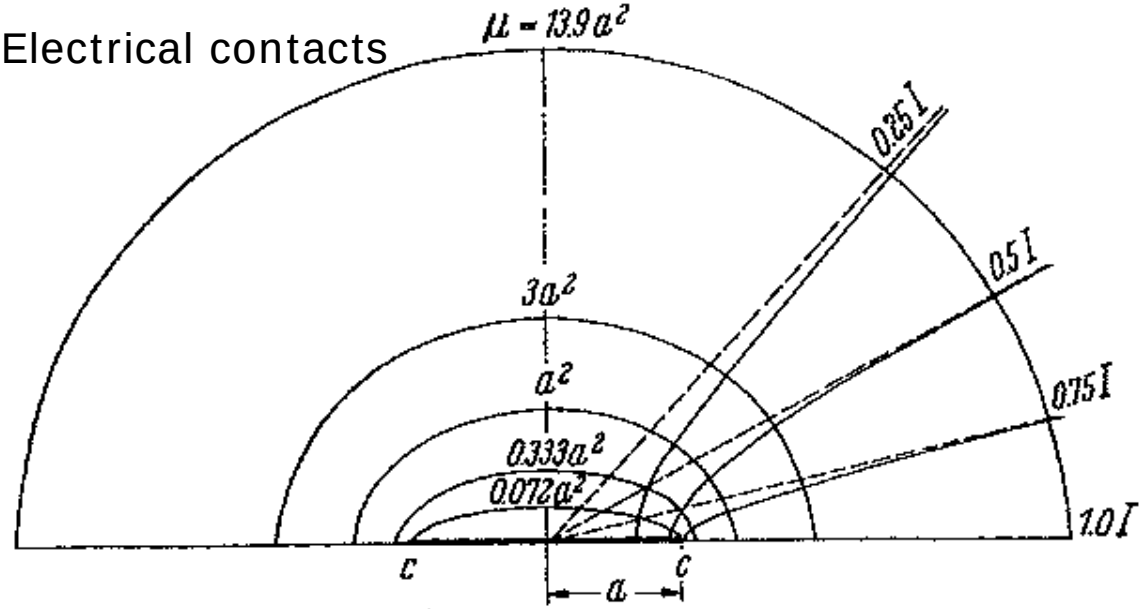


Fig. (4.16). Lines of current flow and equipotential surfaces in the vicinity of a circular a-spot in a symmetric contact. The resistance between two consecutive equipotential surfaces of the figure is 1/6 of the total constriction resistance in one contact member

Parameters important for constriction Resistance

- The contact geometry, in particular roughness
- Contact load, i.e. mechanical pressure
- Materials properties, conductivity, elasticity, ductility (creep and deformation strengths) – temperature is affecting these properties significantly – and current may affect the temperature
- Surface layers (dirt, oxidation products, coatings)

Concluding remarks about contact resistances

- The matter is in the exact details very complicated
- Many example are treated mathematically in Holms book
- In most cases, we have to do own investigation in each single concrete case: measurements, microscopy and modeling

Electrode reaction overvoltage or activation overvoltage

- Activation overvoltage is an unspecific term used when you do not know what you have at hand. There may be many different reasons for electrode reaction rate limitations at an electrode. e.g.:
- adsorption of reactant molecules at the electrode
- bond breaking in the reactant molecule
- surface diffusion of reaction intermediates from the catalytic sites to the three phase boundary (TPB) line
- diffusion of ions through the bulk of electrode particles with mixed conduction
- conduction through or around segregated phases at the surface / at the TPB
- desorption of reaction products
- transfer of ions across the electrode / electrolyte interface
- transfer of electrons from electrode to molecule
- More about this below.

Activation overvoltage

The current density in low temperature electrochemistry is often well described by the Butler - Volmer equation:

$$i = i_0 \cdot \left\{ \exp\left(\frac{(1-\alpha_a) F \cdot \eta}{R \cdot T} \right) - \exp\left(\frac{-\alpha_c F \cdot \eta}{R \cdot T} \right) \right\} \qquad \left[\frac{A}{cm^2} \right]$$

η = E – E_0, the difference between the actual, E = π - ϕ, and the equilibrium, E_0 (i = 0), electrode potential; α_a and α_c are anodic and cathodic symmetry factors, 0 < α < 1

Activation overvoltage

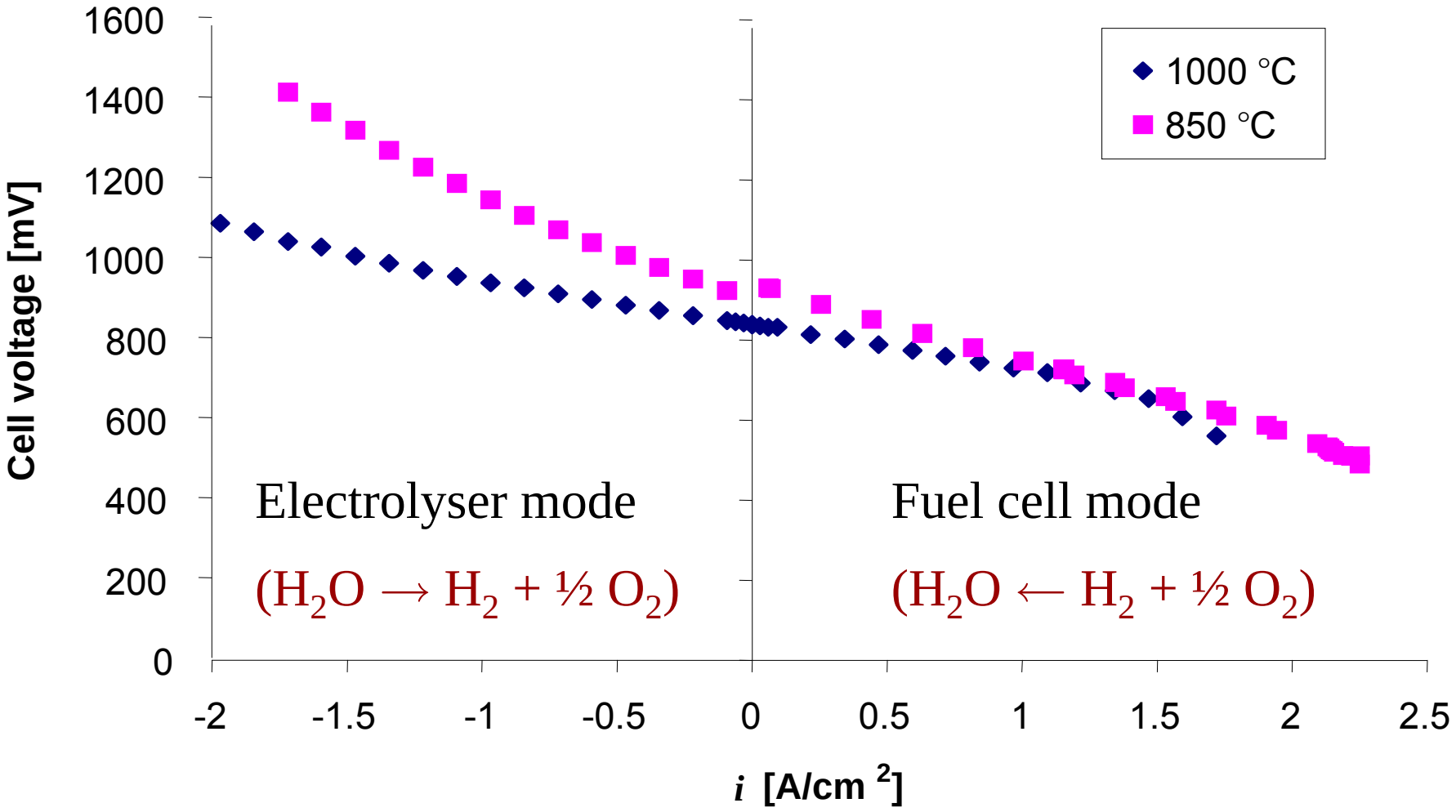
At low overvoltage the Butler-Volmer equation becomes linear

At high overvoltage it gets the same form as the Tafel equation:

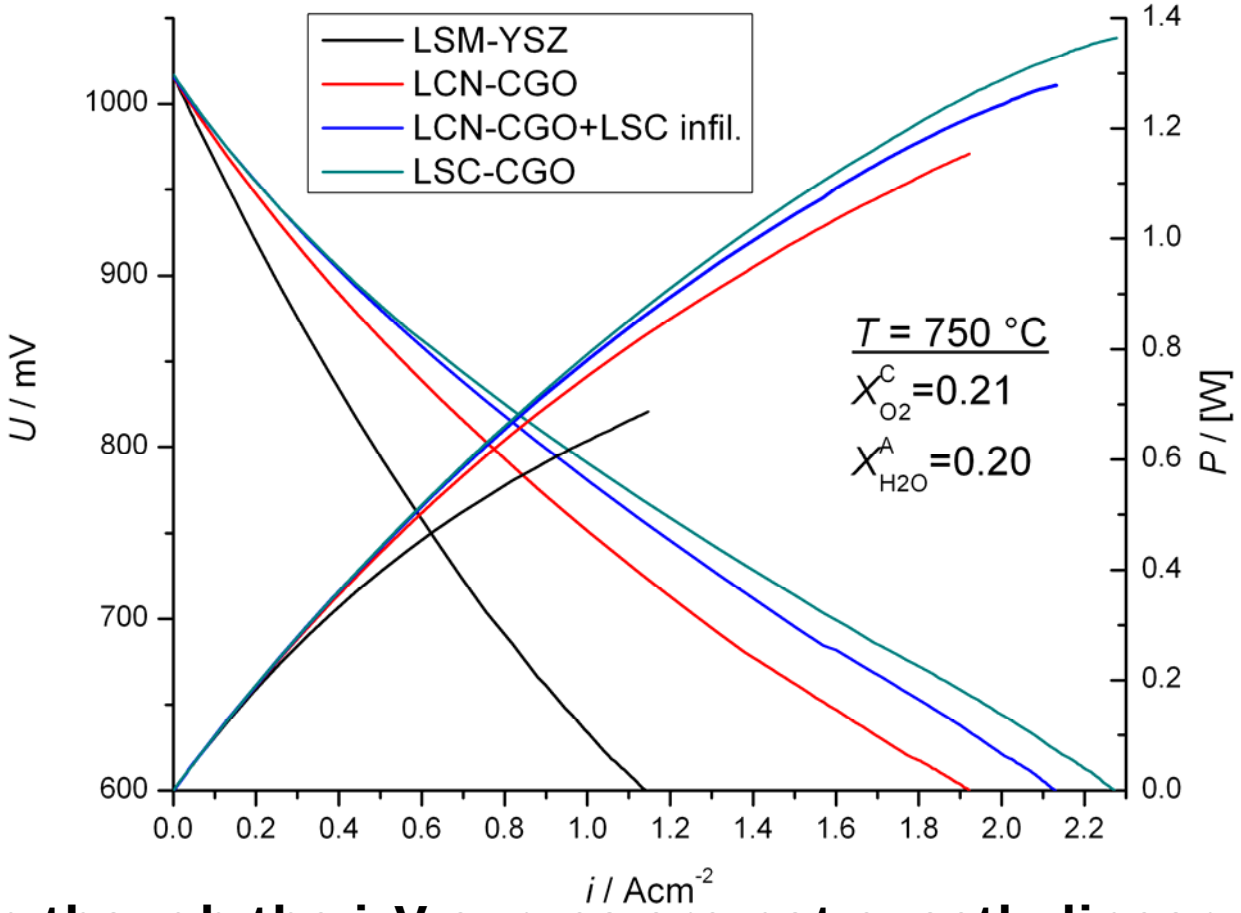
$$\eta = a \pm b \times \log|i|$$

using the absolute value of the current density and the ± sign for anodic and cathodic overpotentials, respectively.

i–V curves for a Risø SOC



i-V curves for other Risø SOCs



Even though the i-V curves are not exactly linear, non of them look exponential in shape. The curve a little in the region of 100 - 150 mV polarisation and then linear again.

Activation overvoltage

- To my best knowledge there is no experimental evidence that charge transfer as described by the Butler - Volmer equation is rate limiting SOC electrode reactions!
- As we will see later, there are evidences for different kinds of rate limiting processes
- Further, the “bottle neck” theory - i.e. only one rate determining step is present at a given condition – is often taken for granted and is actually a prerequisite for the simple Tafel / Butler - Volmer analysis. As we also will see, this is very seldom seen in the case of SOCs.

Gas diffusion overvoltage

- If the diffusion of gas through a stagnant layer of gas either outside an electrode or inside a thick porous electrode then a gas diffusion overvoltage appears. the size is given by the difference in the equilibrium potentials determined by the Nernst equation applied to: 1) the OCV situation, and 2) the gas composition at the electrode surface in the situation with a current load high enough to change the gas composition at the electrode-electrolyte interface.

- More about this later.

Gas conversion overvoltage

- **Gas conversion overvoltage occurs when the gas concentration (partial pressure) cannot be maintained in the electrode compartment. When this is the case, a contribution to the change in electrode potential will appear as given by the difference in the equilibrium potentials determined by the Nernst equation applied to: 1) the OCV situation, and 2) the situation with a current load high enough to change the gas composition in the electrode compartment.**

- **Much more about this later.**

Measurements of electrolyte resistance, reaction resistance and electrode overvoltage by EIS

- Both measurements of cell voltage vs current density curve (i - V curves) and electrochemical impedance spectroscopy (EIS) are necessary in order to characterise an electrode.

- The i - V curves are necessary in order to prove the actual electrode or cell performance. They are simple to measure, but usually very difficult to interpret.

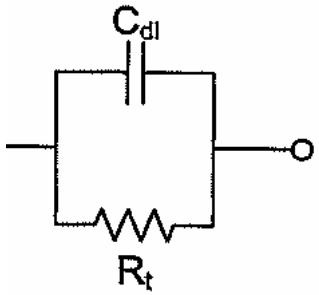
- The single EIS spectrum is also difficult to interpret, but using suitable strategy the EIS is a most valuable tool

Equivalent circuit

- The total current is the sum of two currents

$$i = i_C + i_F$$

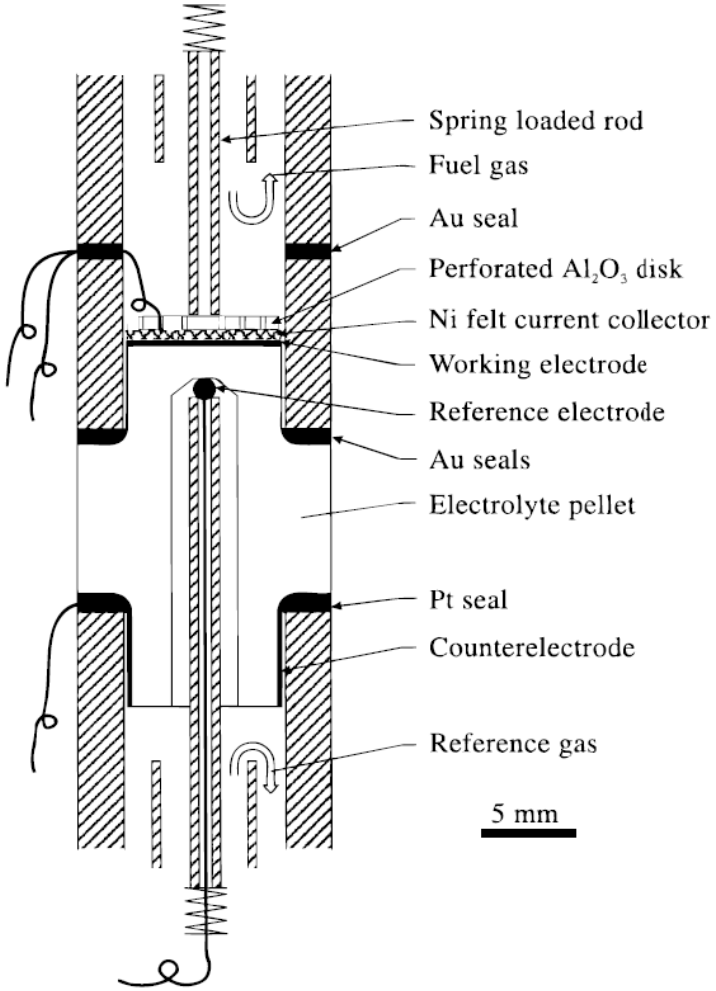
- Therefore, the simples equivalent circuit for the electrode is a parallel connection between a capacitor and a resistor:



- This gives a semi-circle in the EIS plot

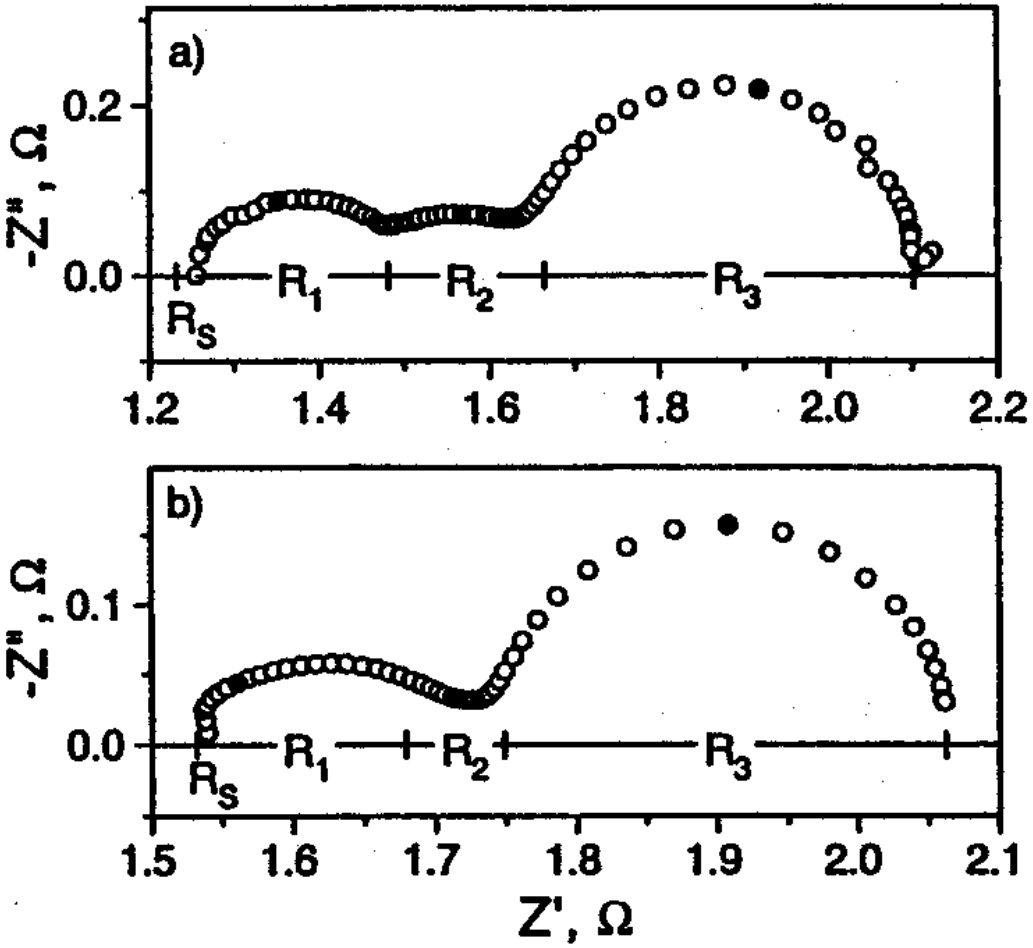
- We will use the Ni/YSZ/H_2/H_2O electrode as example

Risø three electrode (3-E) set-up



Primdahl and Mogensen. *JES* **146**, 2827 (1999)

3E-set-up EIS on H_2 / 3 % H_2O / Ni-YSZ at 1000 °C.

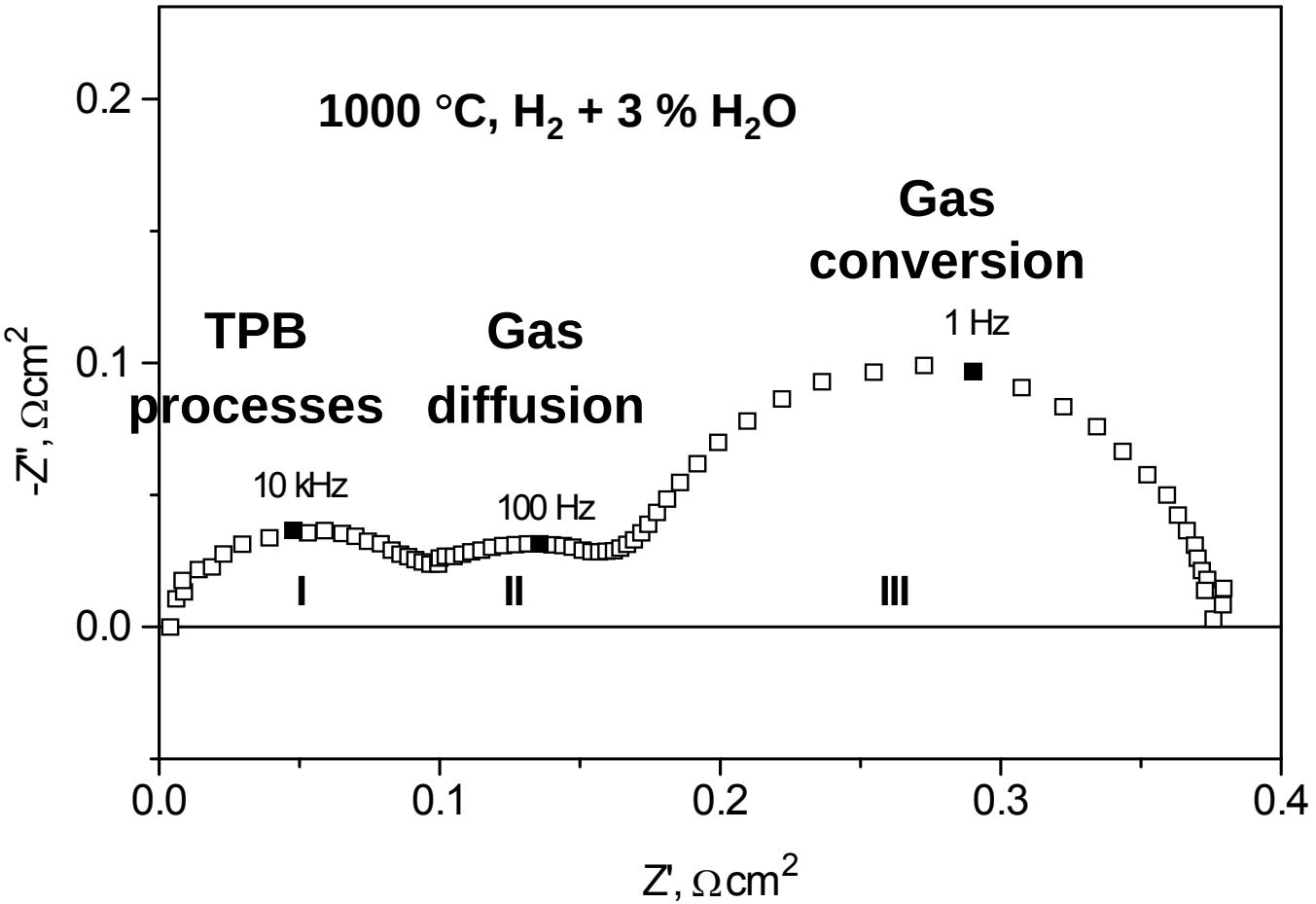


1Hz

1 Hz

a) 50 / 50 vol % fine powder Ni / YSZ,
b) Risø more "normal" Ni / YSZ

Interpretation

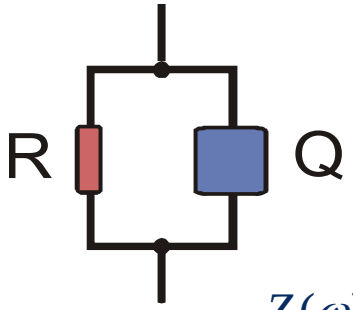


TPB related processes

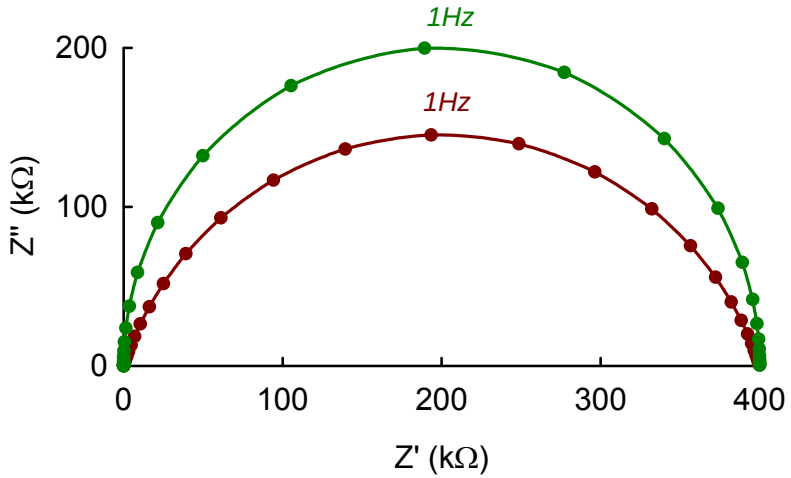
- The details of the electrode processes of both anode and cathode are still under debate, and thus, no clear-cut explanation can be given yet.
- Examples of measurements on cells follows
- Some of the hypothesis about the mechanisms will be given at the end of this lecture for both anode and cathode.

Equivalent circuits

- An equivalent circuit can consist of several, combined elements, like resistors, inductors and capacitors



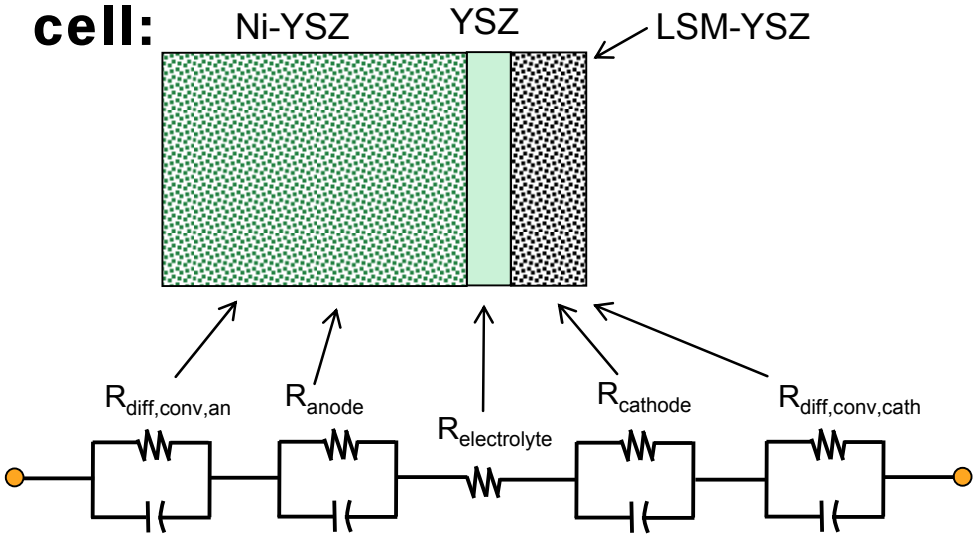
$$Z(\omega) = \left(R^{-1} + Q \cdot (i\omega)^{n} \right)^{-1}$$

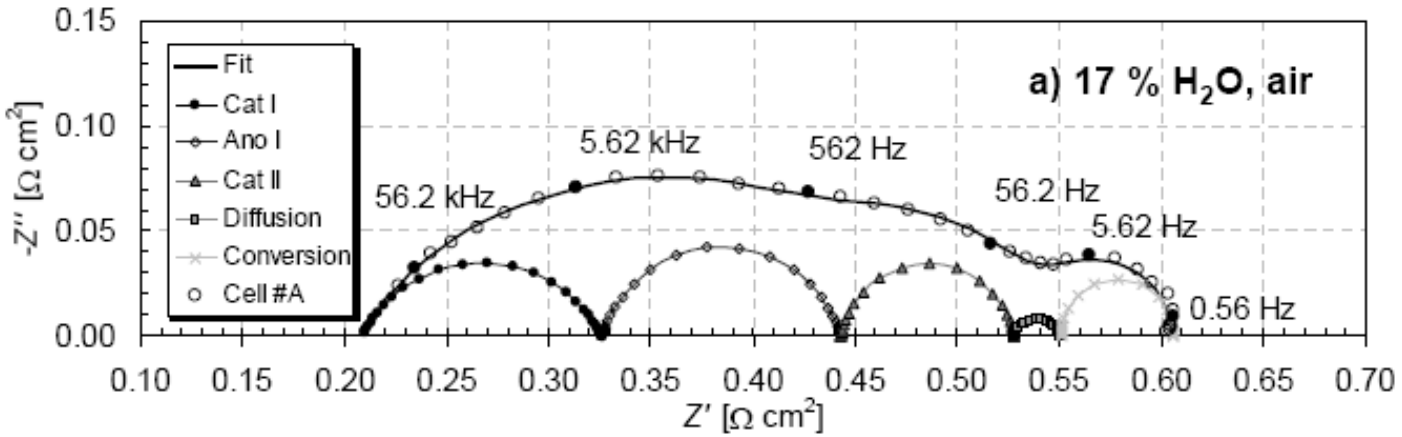


- An equivalent circuit can be developed to describe the system and separate the magnitude of the physical processes:
  - Several impedance spectra are required, recorded at e.g. different temperatures and gas compositions
  - EIS is not a 'stand alone' technique; more information is required about the system, obtained from e.g. electron microscopy

Equivalent circuits

- **Example of an equivalent circuit for a solid oxide fuel cell:**

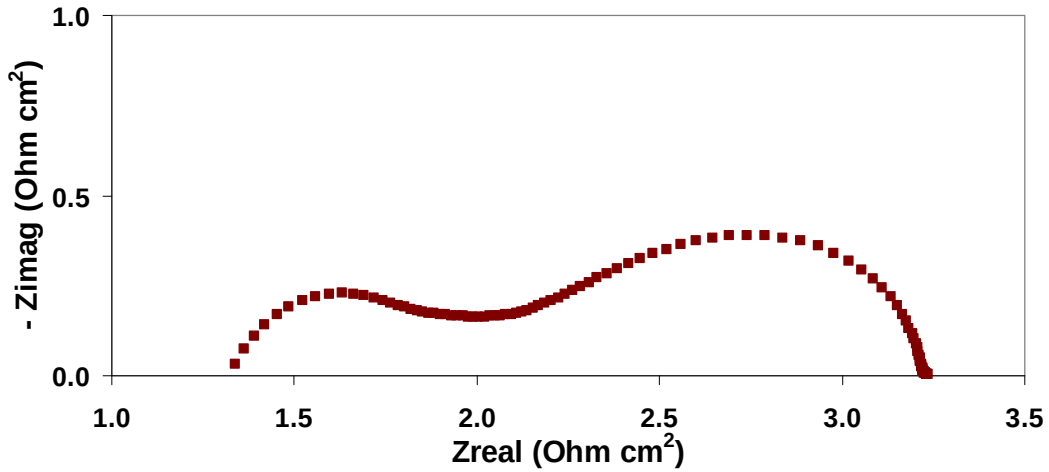




Ramos et al. 2008, ECS Transactions 13 235

Equivalent circuits

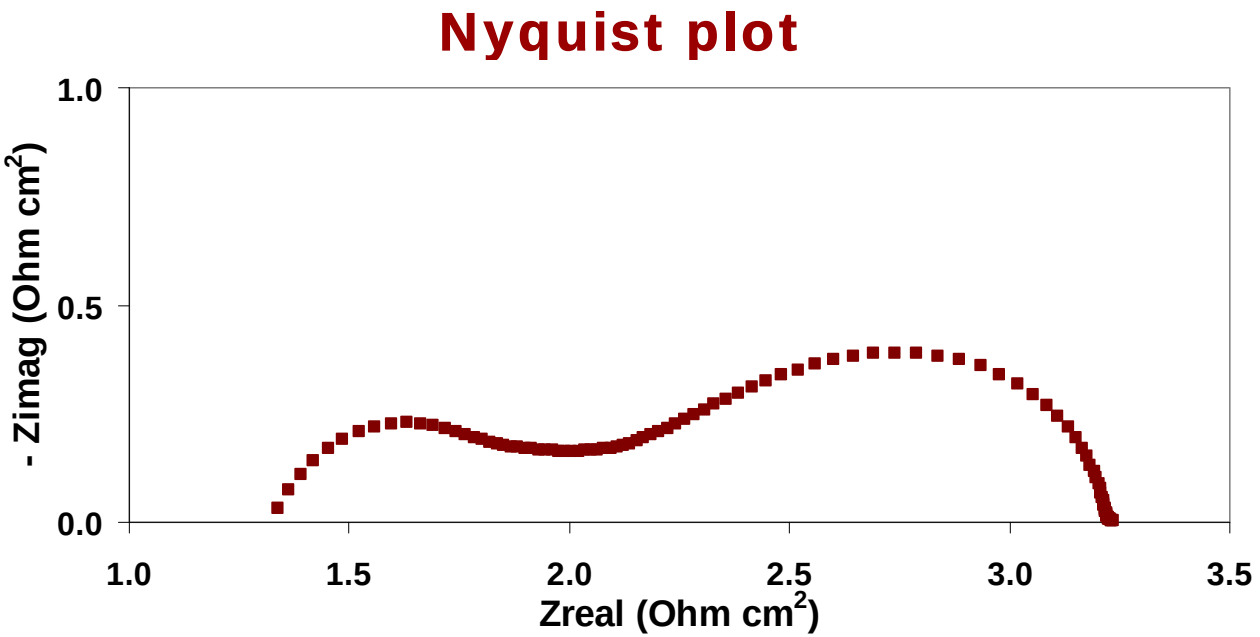
- Often, impedance spectra are complex as they describe several, (partially) overlapping physical processes.



- Three approaches can help to develop the equivalent circuit of a complex system:
  - Plotting the spectra in different graphical forms
  - Analysis of differences in impedance spectra
  - Distribution of relaxation times (DRT) analysis of high quality impedance spectra

Graphical representations of EIS spectra

- **Different, complementary information can be obtained by plotting the data in different forms, for example:**

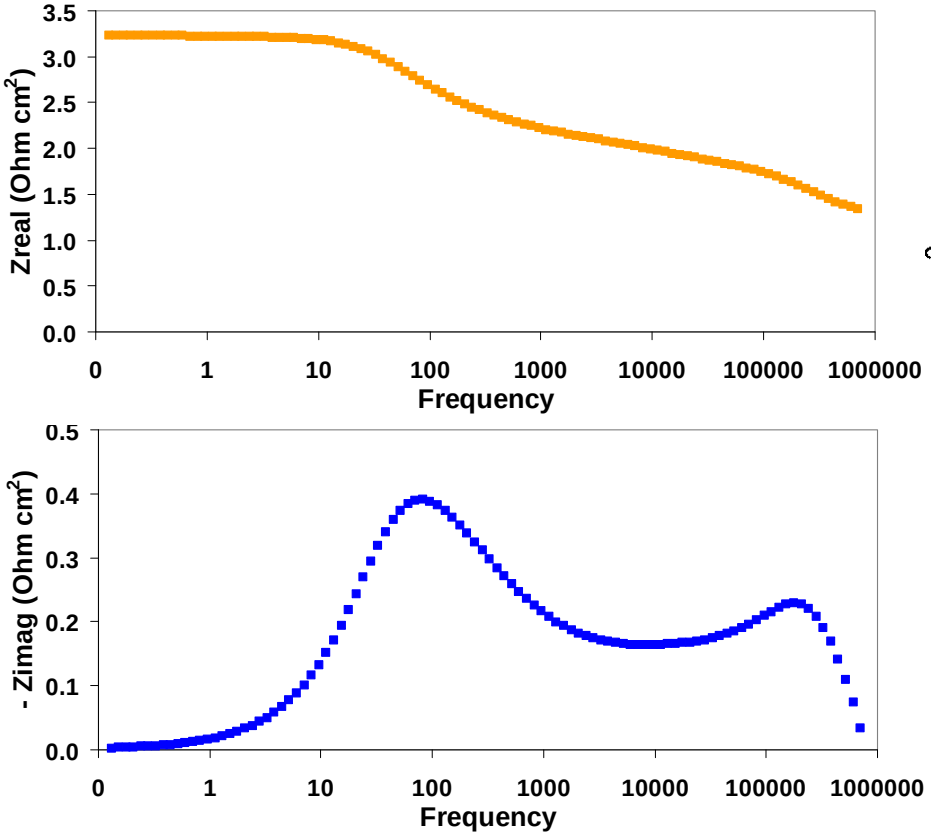


Orazem et al. 2006, J. Electrochem. Soc. 153 B129

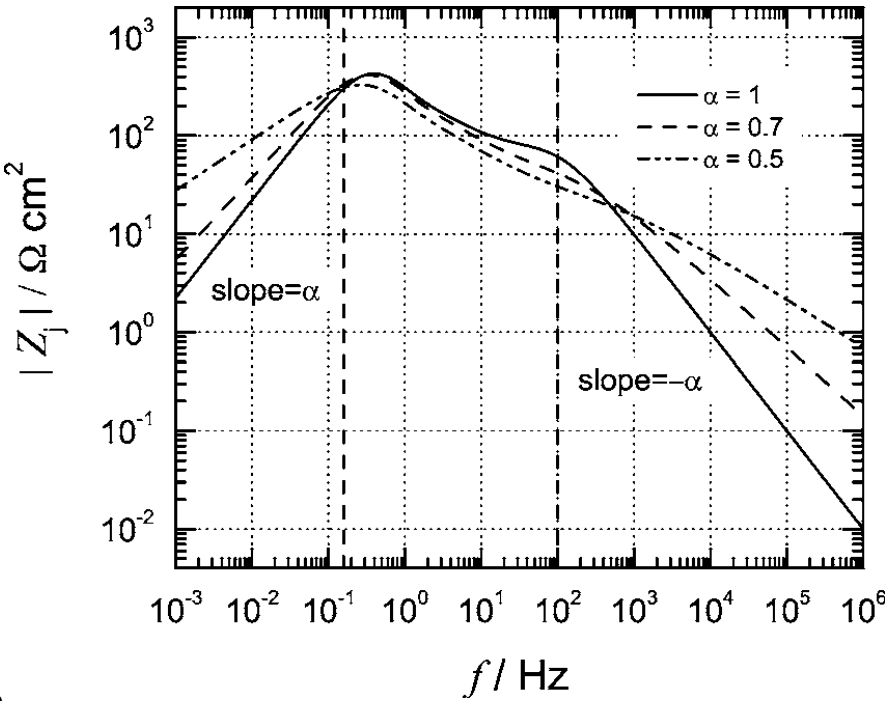
Graphical representations of EIS spectra

- **Different, complementary information can be obtained by plotting the data in different forms, for example:**

Bode plots of impedance:



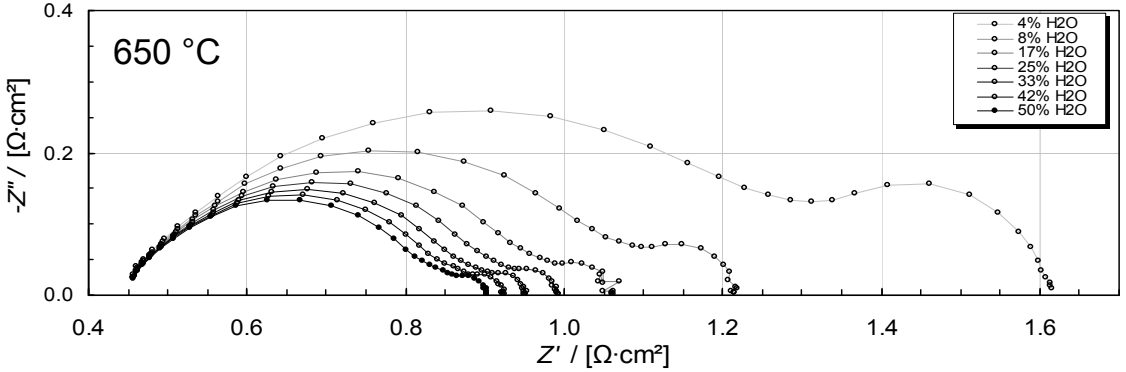
'logaritmic' Bode Plot

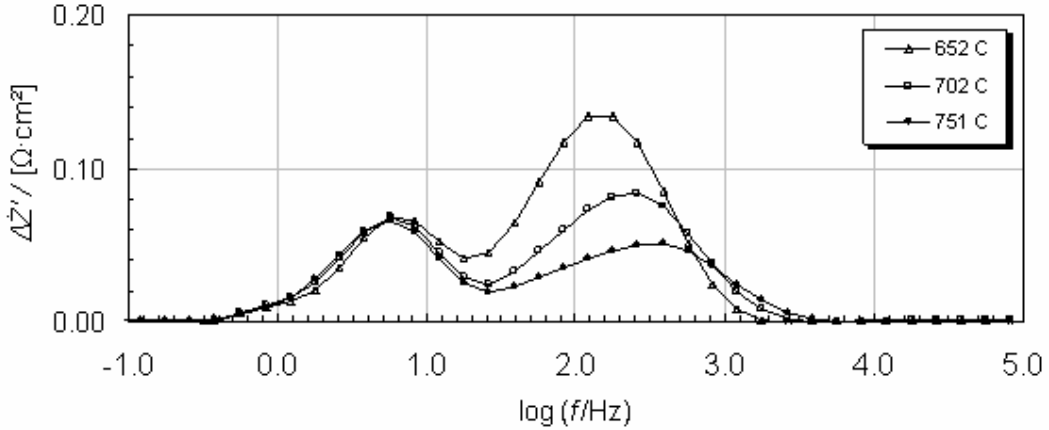


Orazem et al. 2006, J. Electrochem. Soc. 153 B129

Analysis of differences in impedance spectra (ADIS)

- An impedance spectrum often changes when the temperature or gas composition is changed. When analysing the differences between spectra, the number and nature of the changes can be analysed

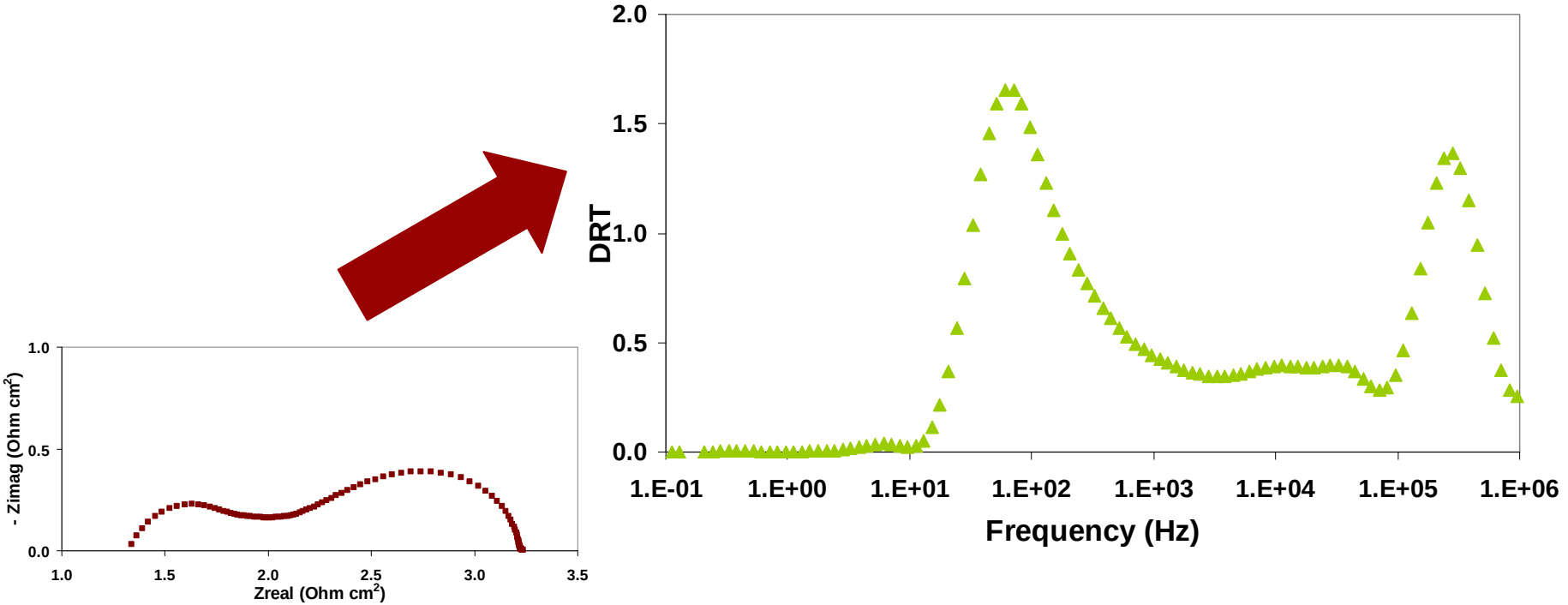




Jensen et al. 2007, J. Electrochem. Soc. 154 B1325
Hjelm et al. 2008, ECS Transactions 13 285

Distribution of relaxation times (DRT)

- Distribution of relaxation times is gained by a Fourier transform of the impedance data, giving a clearer picture of the number of physical processes and their nature

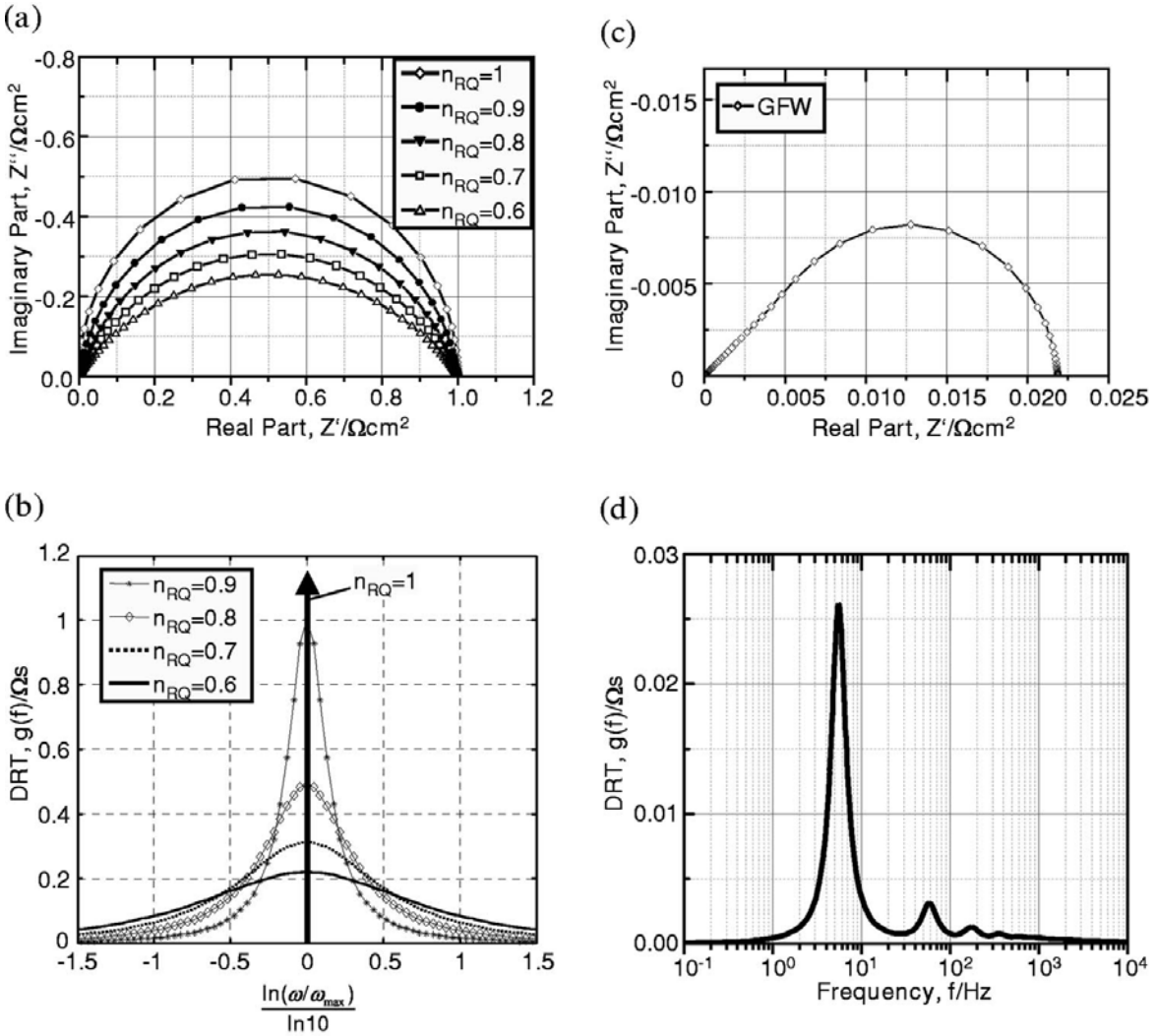


Schichlein et al. 2002, J. Appl. Electrochem. 32 875

Distribution of relaxation times (DRT)

Nyquist representation

DRT representation

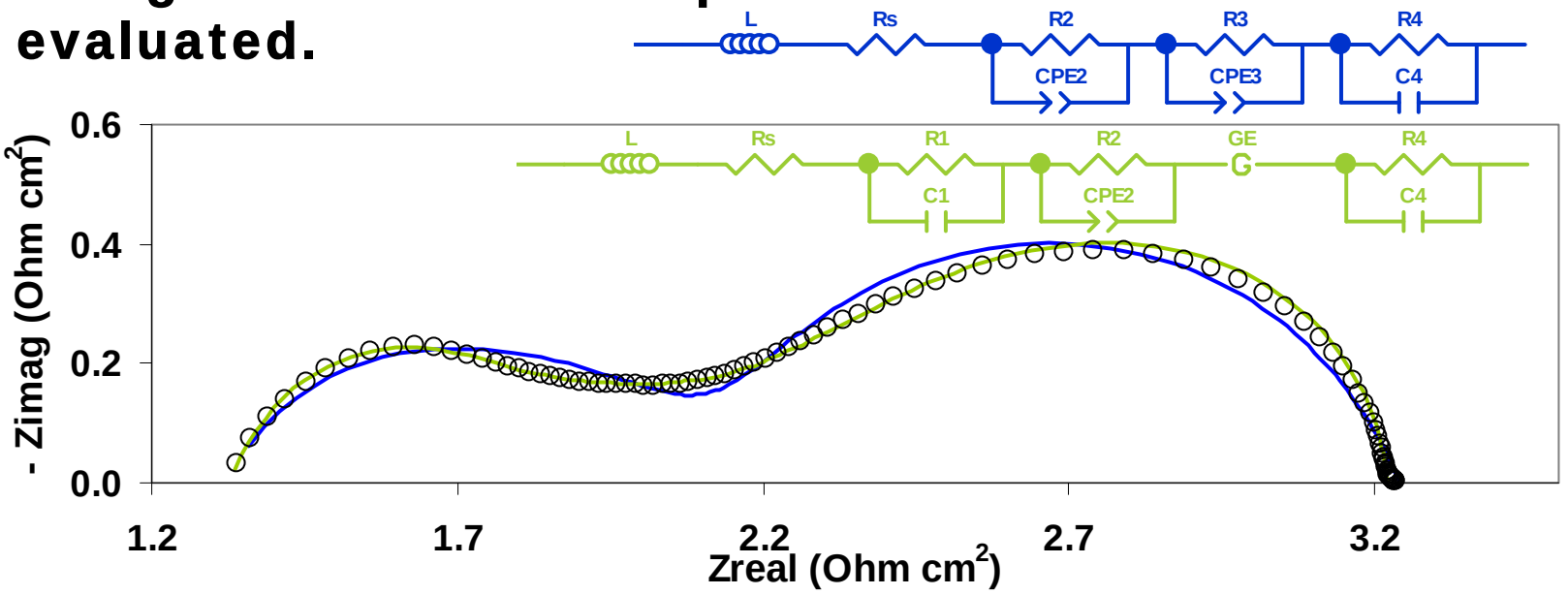


Leonide et al. 2008, J. Electrochem. Soc. 155 B36

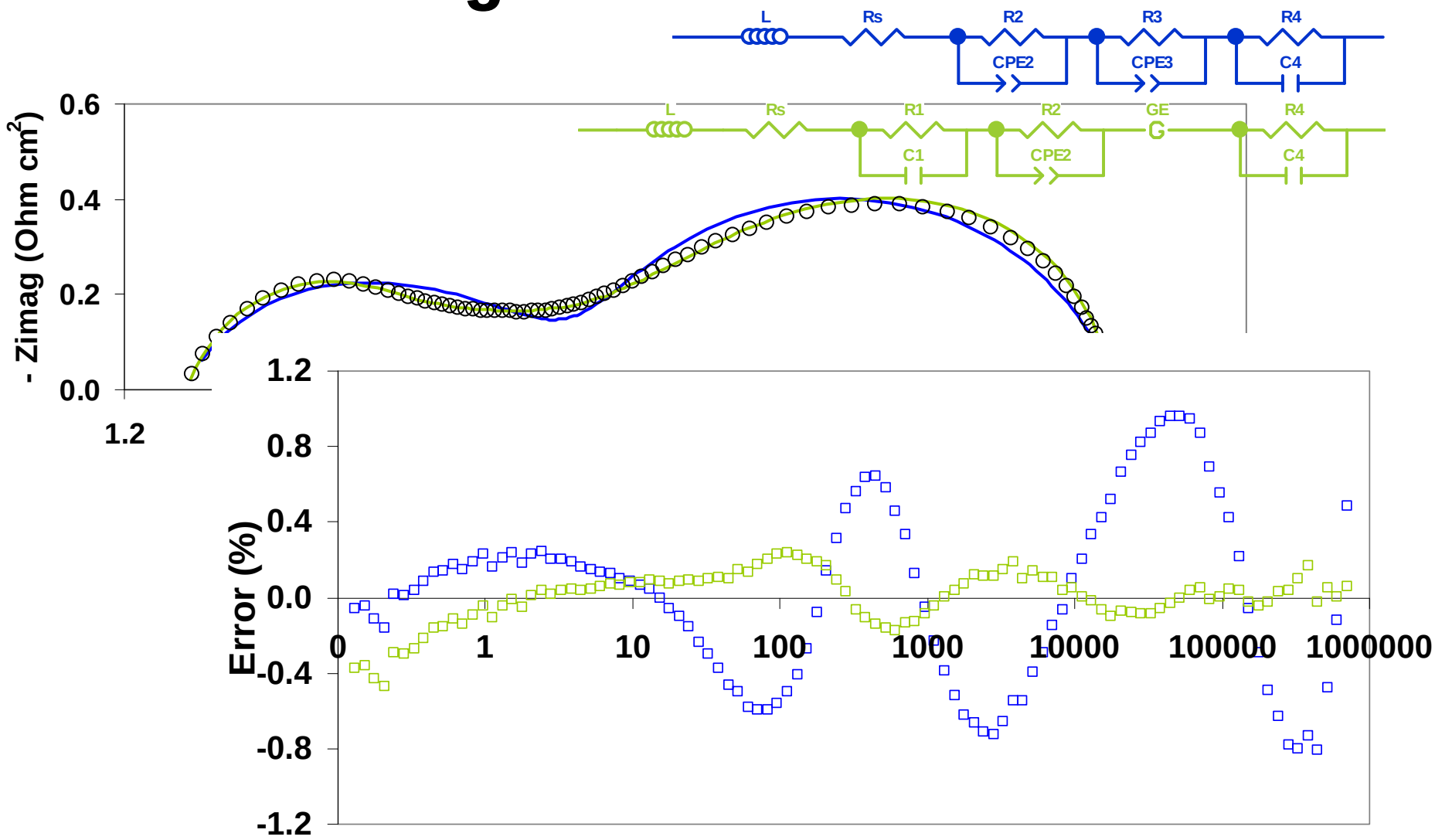
CNLS fitting

- When an equivalent circuit has been developed, the magnitudes of each of the elements can be calculated by CNLS fitting.

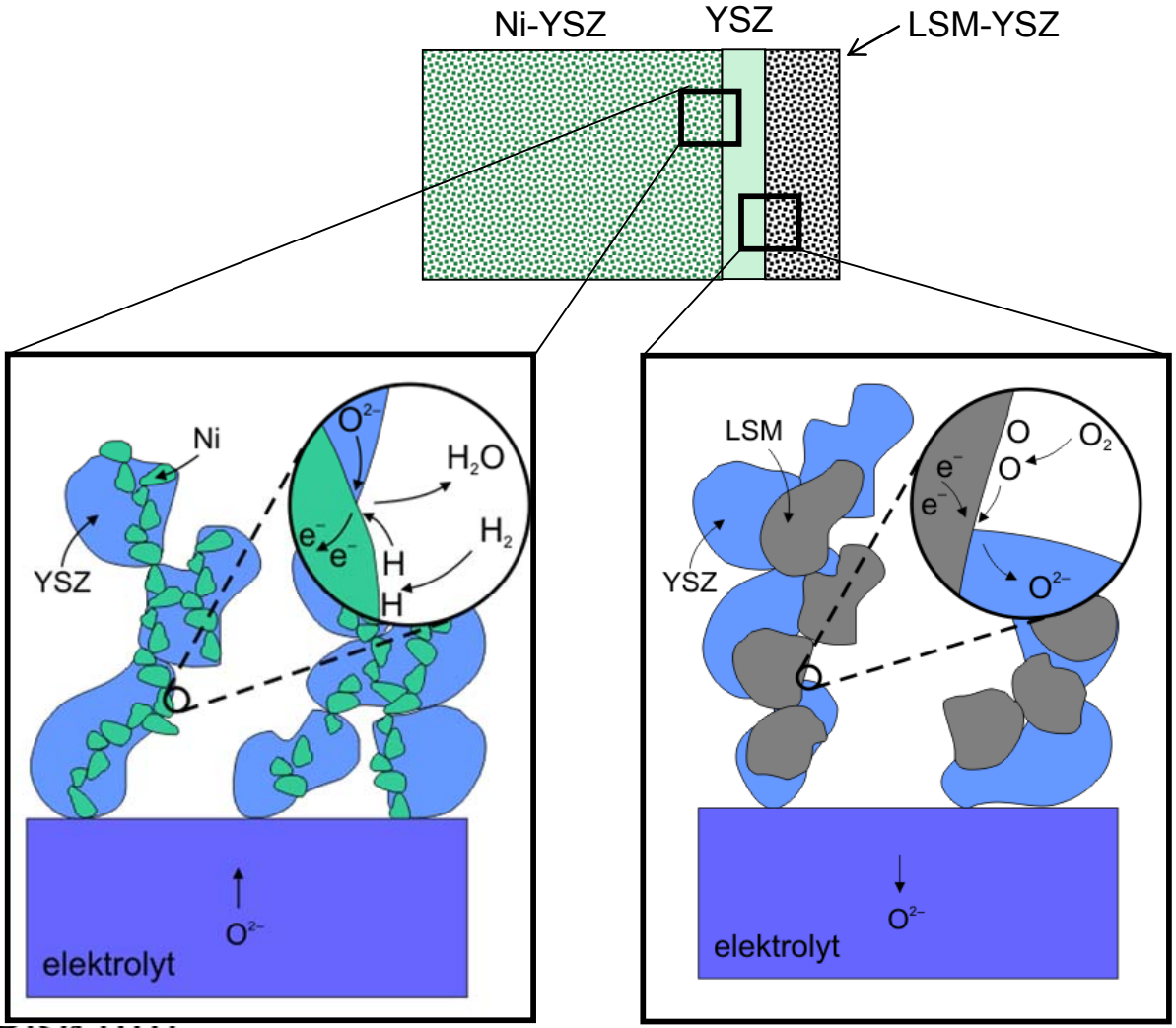
- By plotting the calculated values from the CNLS fitting, the 'goodness' of the equivalent circuit can be evaluated.

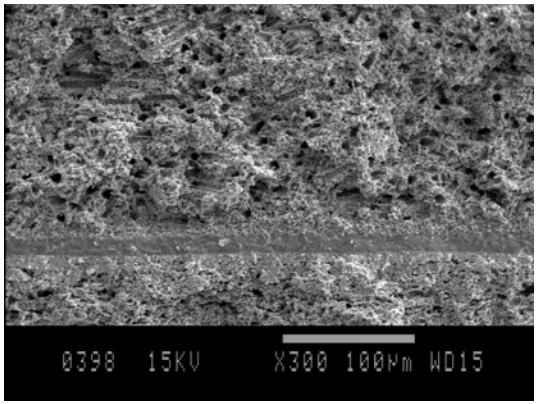


CNLS fitting



Degradation / deactivation of symmetrical solid oxide cells



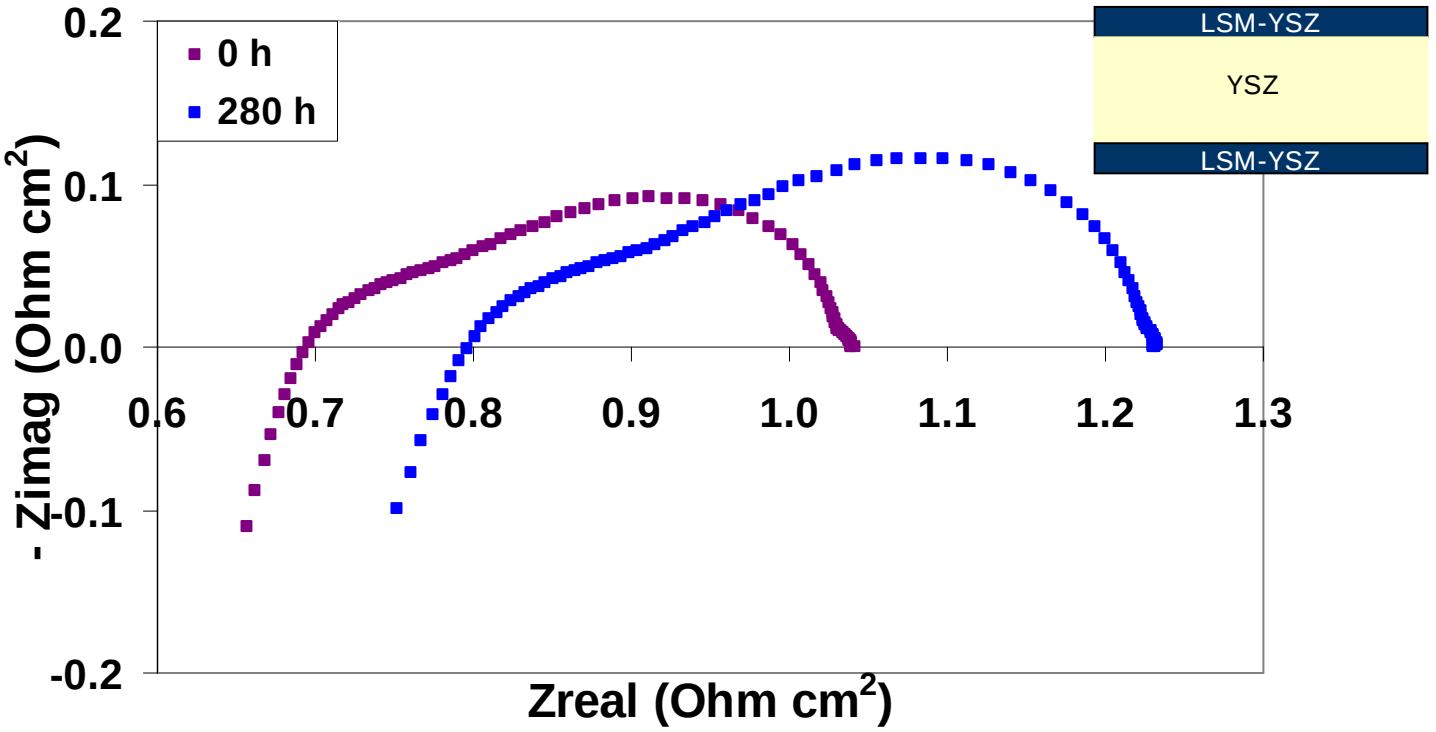


Solid oxide cells:

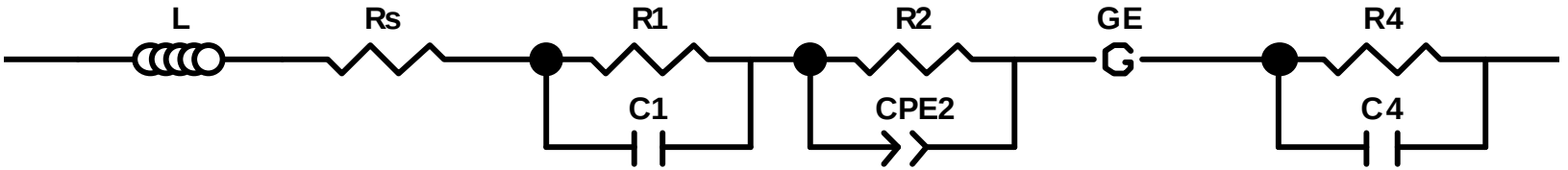
Many processes (mass & charge transfer)

Porous, composite electrodes

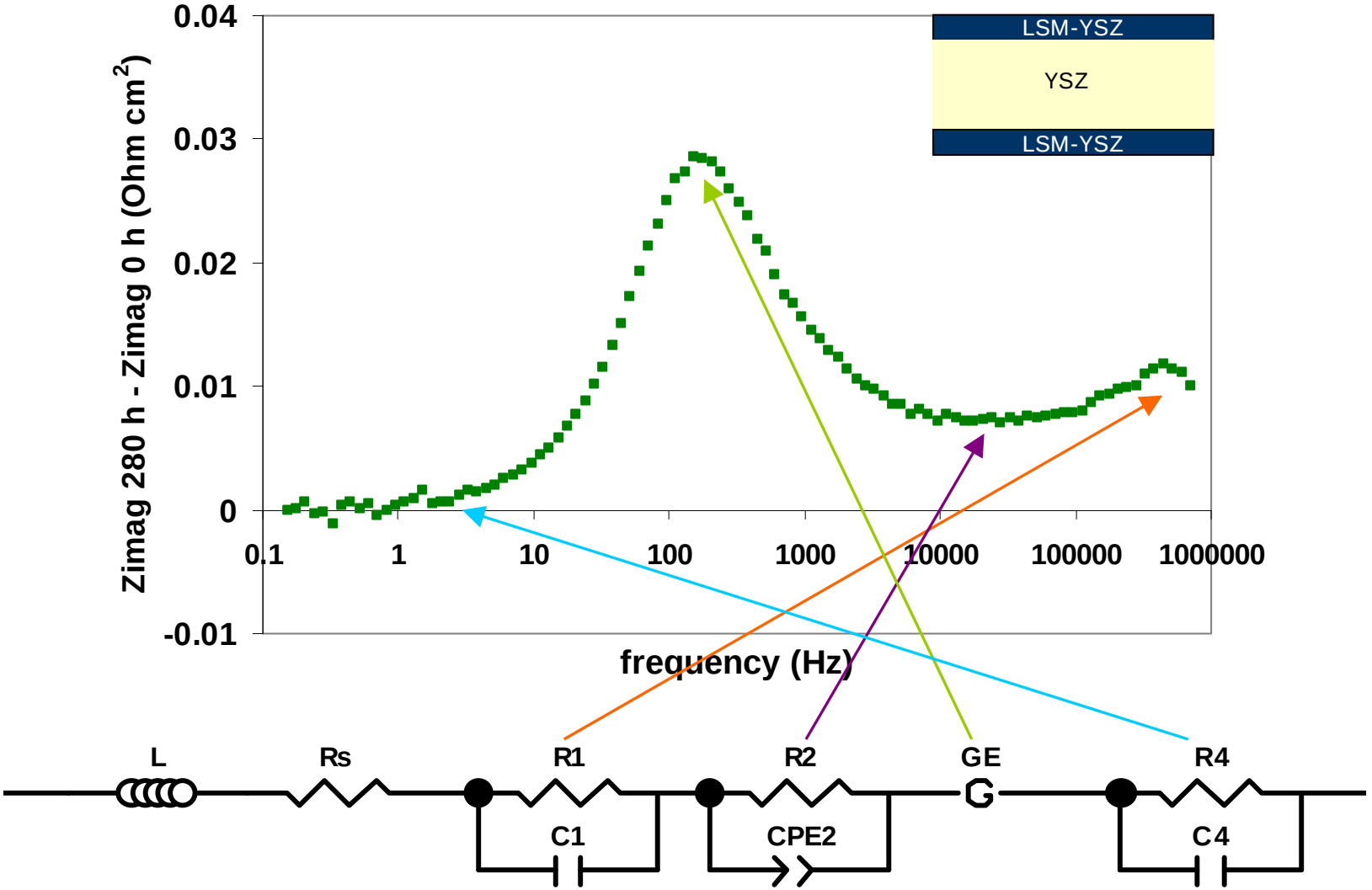
Degradation / deactivation of symmetrical solid oxide cells



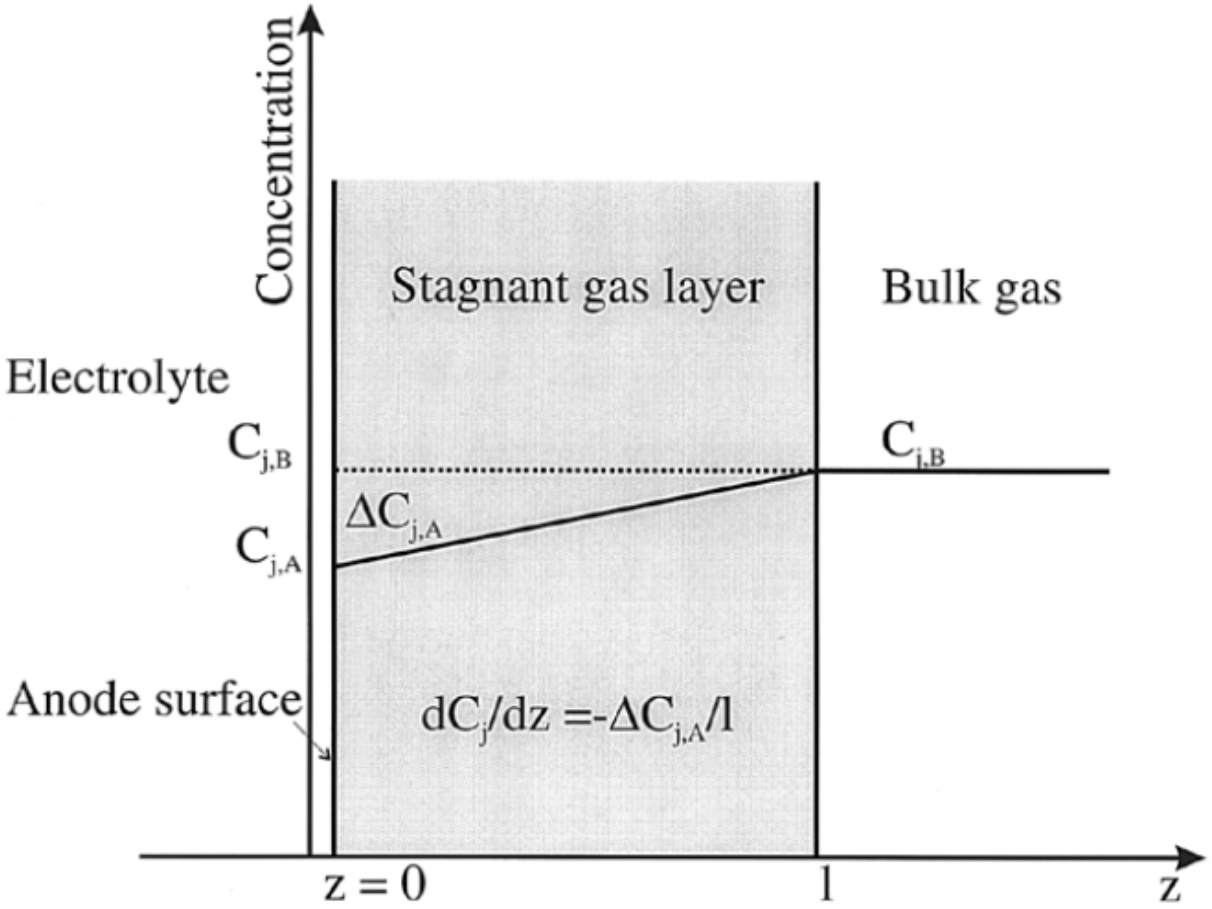
Equivalent circuit:



Degradation / deactivation of symmetrical solid oxide cells

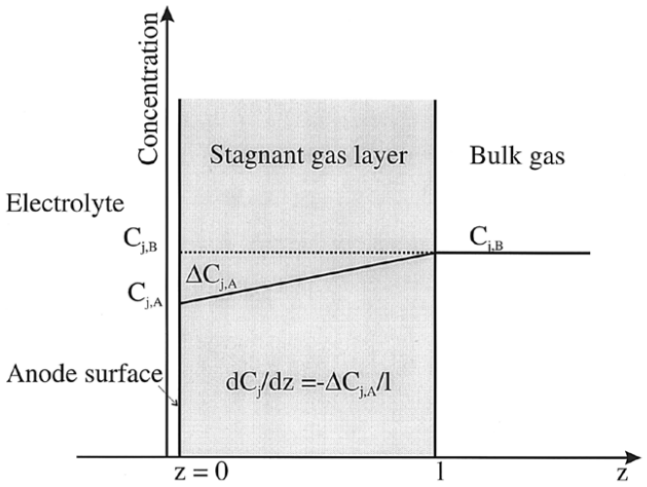


Gas Diffusion Impedance



Primdahl and Mogensen. *JES* **146**, 2827 (1999)

Gas Diffusion Impedance



Fick's first law of diffusion:

$$j_{\mathrm{j,A}} = -D_{\mathrm{Eff}} \left.\frac{dC_{\mathrm{j,A}}}{dz}\right|_{z=0}$$

$$j_{\mathrm{j,A}} = \frac{i}{2F}$$

$$\Delta C_{\mathrm{H_2O,A}} = \frac{li}{2FD_{\mathrm{Eff}}}$$

$$D_{12} = \frac{10^{-7} T^{1.75} \sqrt{\frac{1}{M_1} + \frac{1}{M_2}}}{P\left(\sqrt[3]{v_1} + \sqrt[3]{v_2}\right)^2}$$

$$E = E_0 + \frac{RT}{nF} \ln \frac{P_{\mathrm{H_2O}}}{P_{\mathrm{H_2}} \sqrt{P_{\mathrm{O_2}}}}$$

Primdahl and Mogensen. *JES* **146**, 2827 (1999)

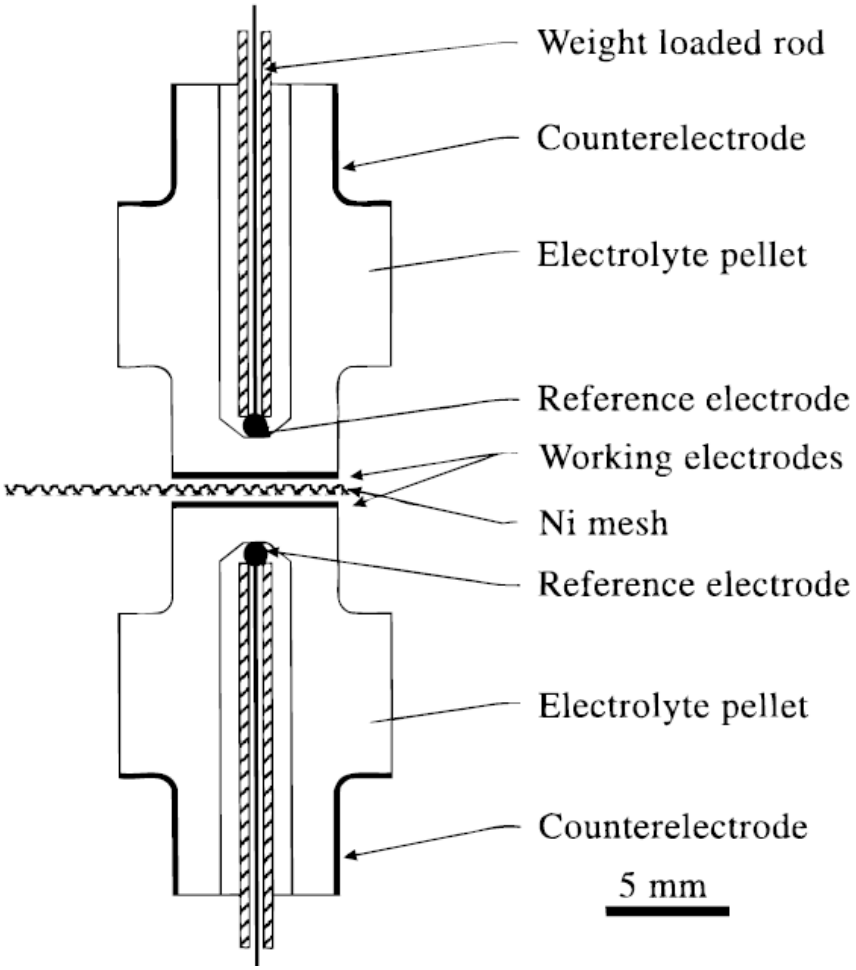
Gas Diffusion Impedance

$$R_D = \frac{\eta_D}{i} = \left(\frac{RT}{2F}\right)^2 \frac{l}{PD_{Eff}} \left(\frac{1}{X_{H_2,B}} + \frac{1}{X_{H_2O,B}}\right)$$

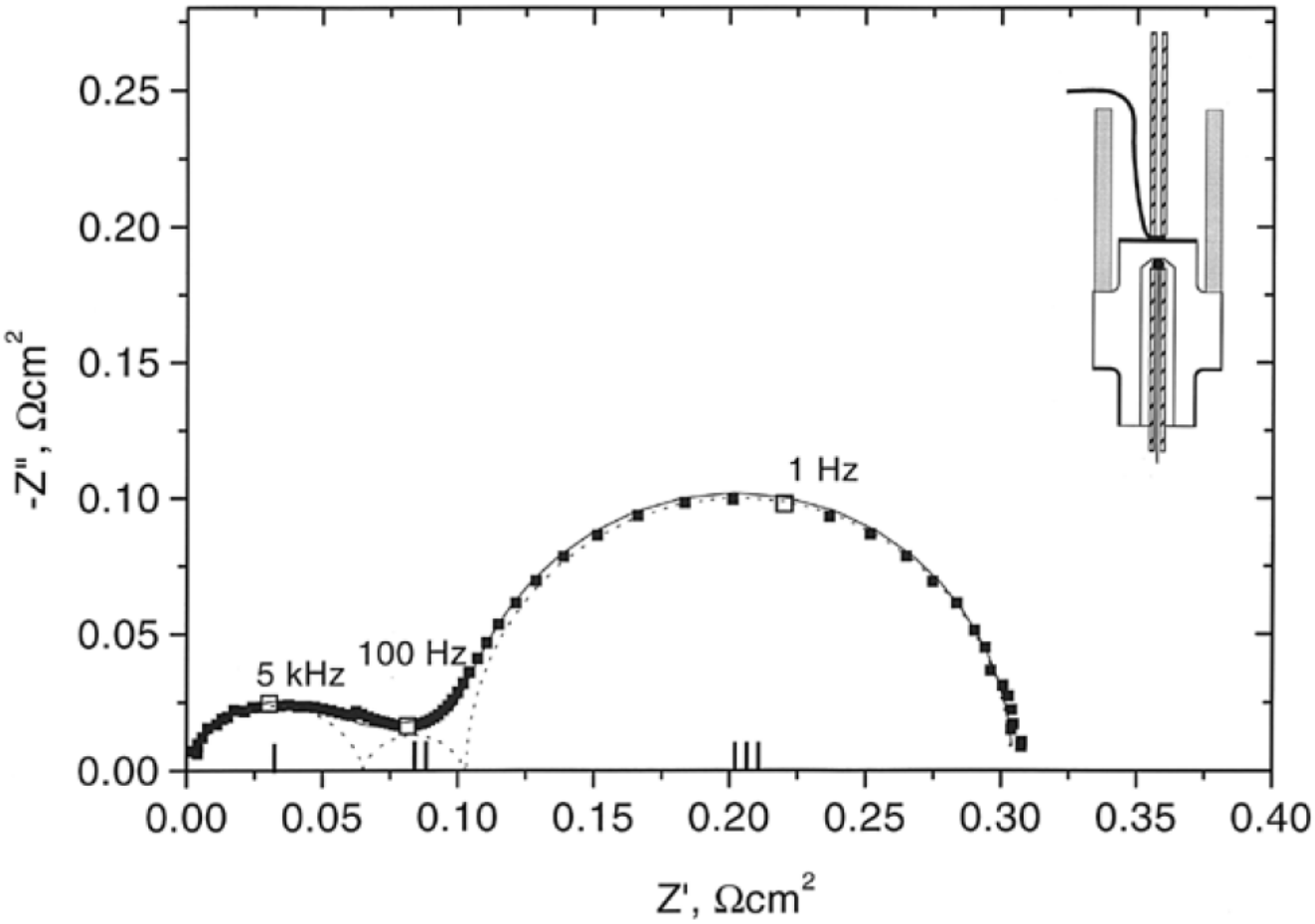
$$\tau = \delta^2 / D_{Eff}$$

$$Z_d = \frac{\eta_d}{i} = \frac{RT\delta}{n^2F^2} \left(\sum \frac{\nu_j^2}{D_j c_j^o} \frac{\tanh\left[\delta\sqrt{\frac{j\omega}{D_j}}\right]}{\delta\sqrt{\frac{j\omega}{D_j}}} \right)$$

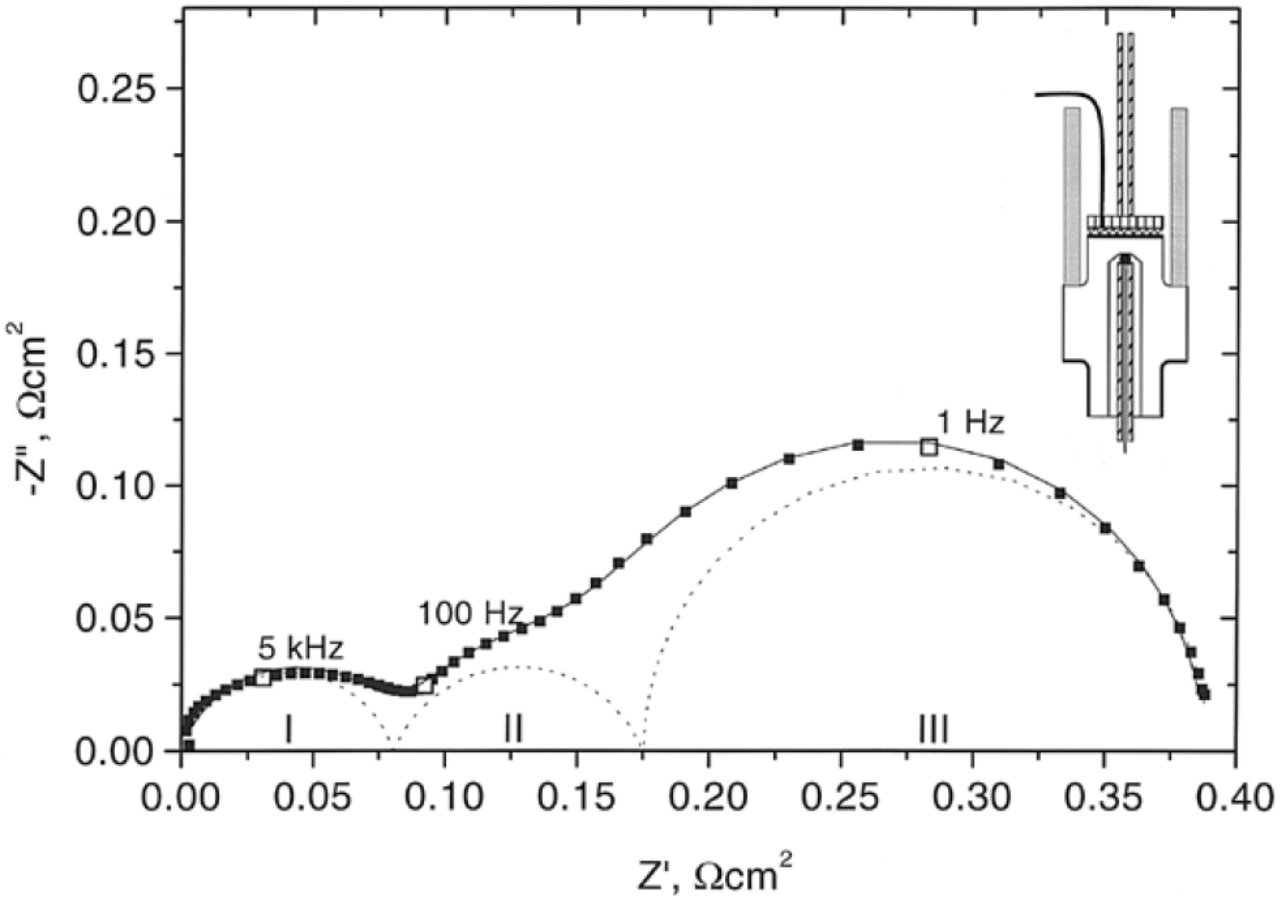
Gas Diffusion Impedance



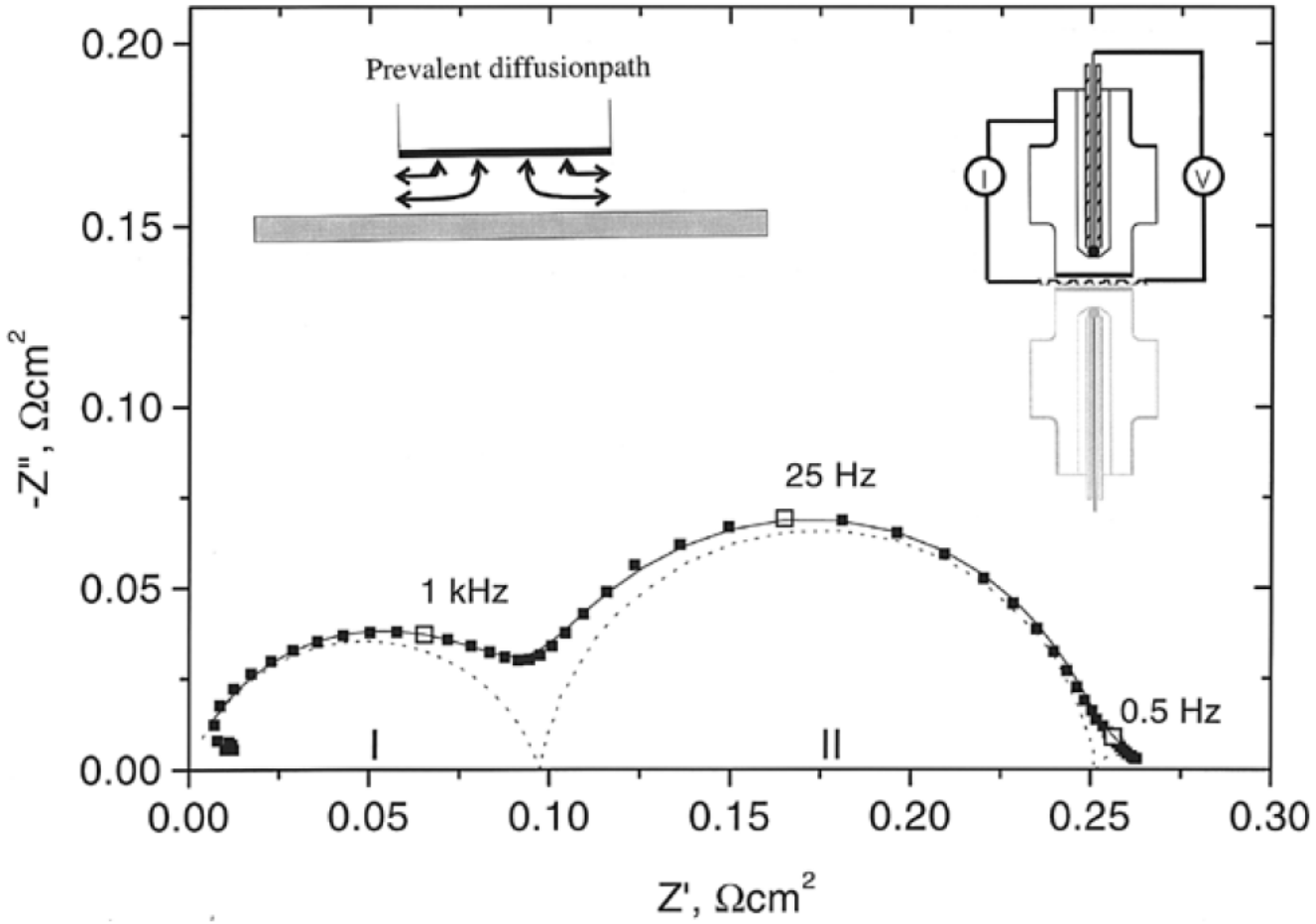
Gas Diffusion Impedance



Gas Diffusion Impedance



Gas Diffusion Impedance



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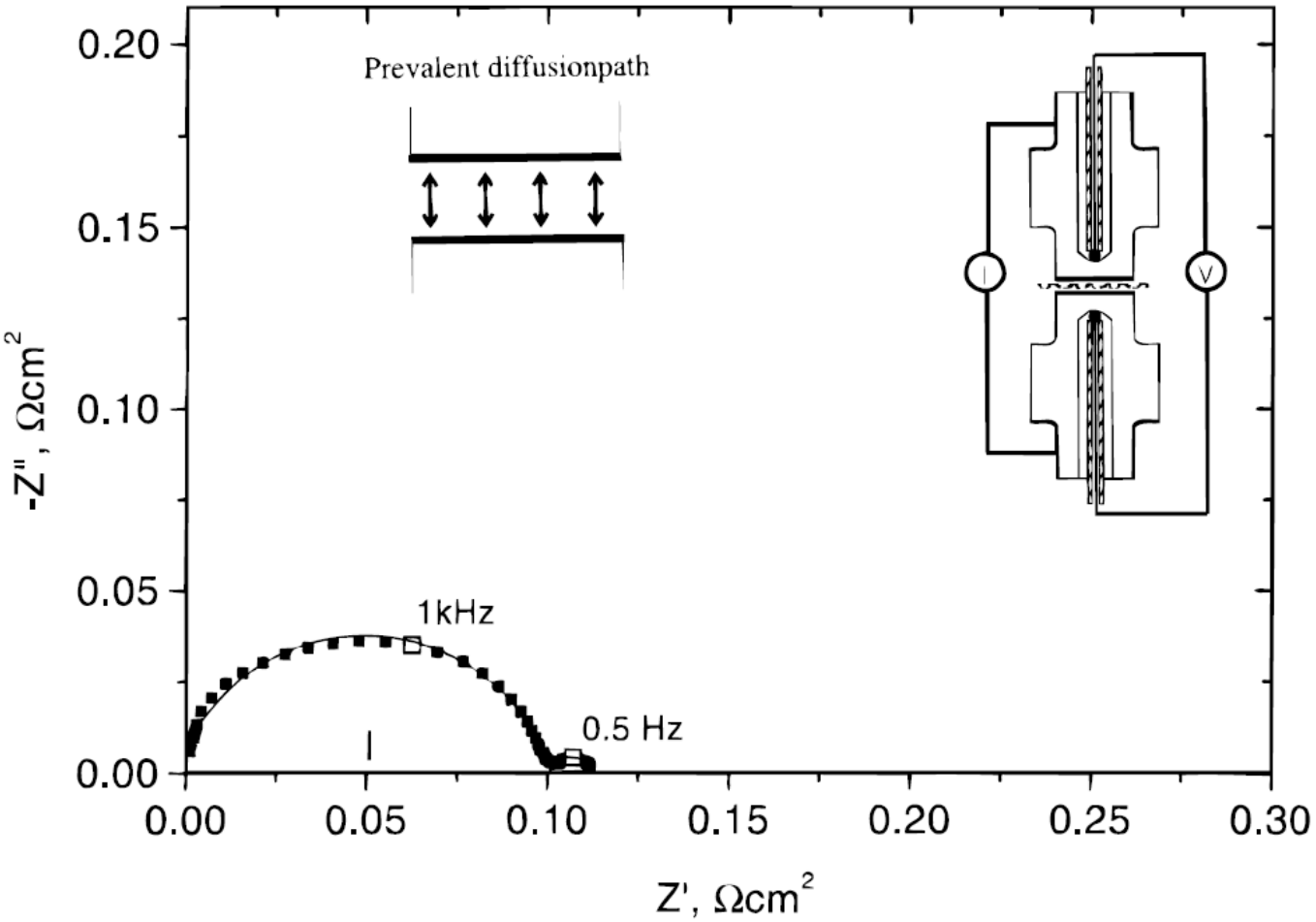
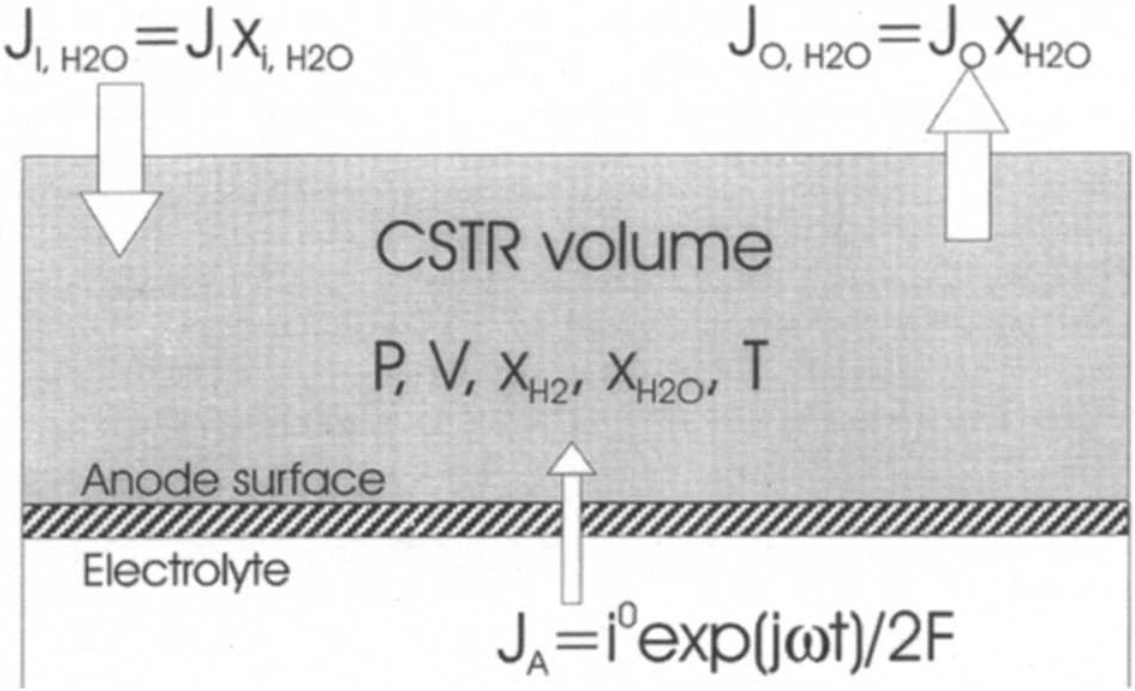


Primdahl and Mogensen. *JES* **146**, 2827 (1999)

Gas Conversion Impedance

Primdahl and Mogensen. *JES* **145**, 2431 (1998)

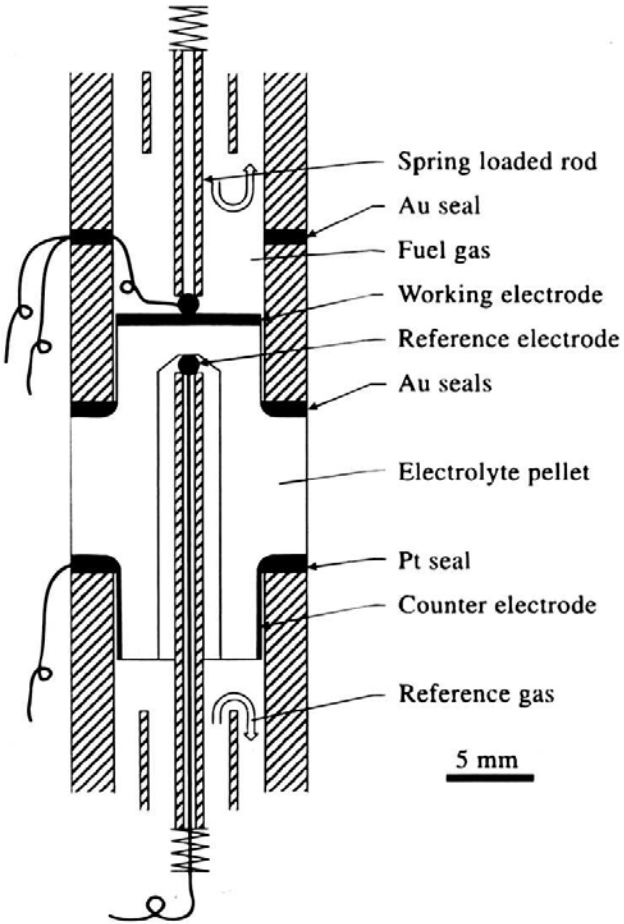


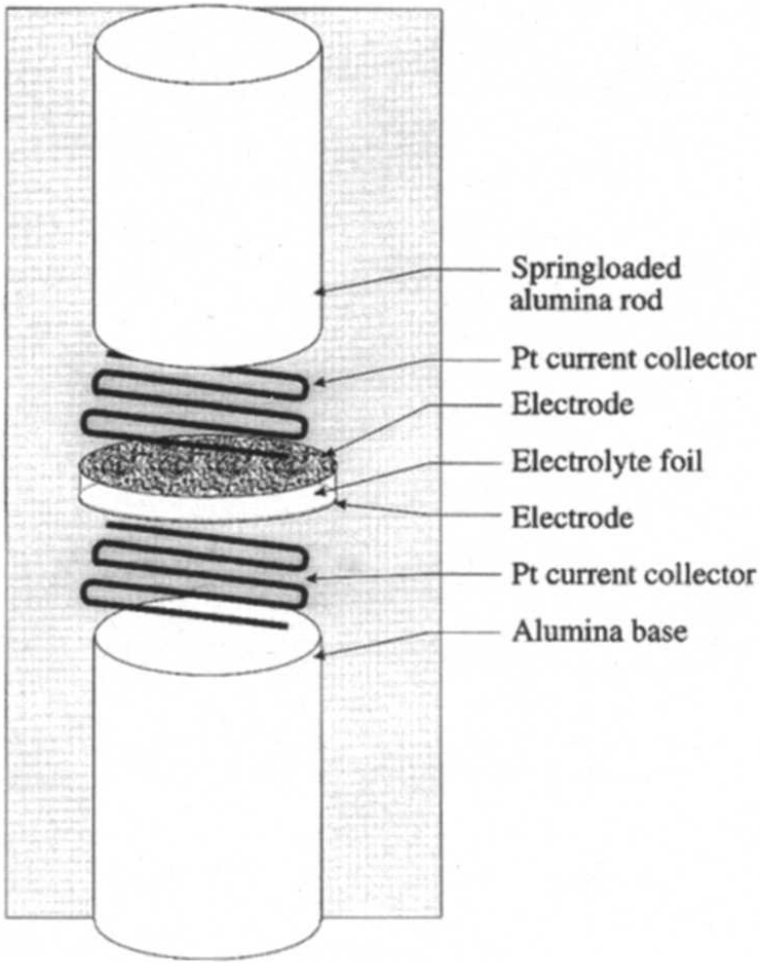
$$J_I = J_O + J_A$$

$$H_2 + O^{--} \rightarrow H_2O + 2e^-$$

Gas Conversion Impedance

Primdahl and Mogensen. *JES* **145**, 2431 (1998)





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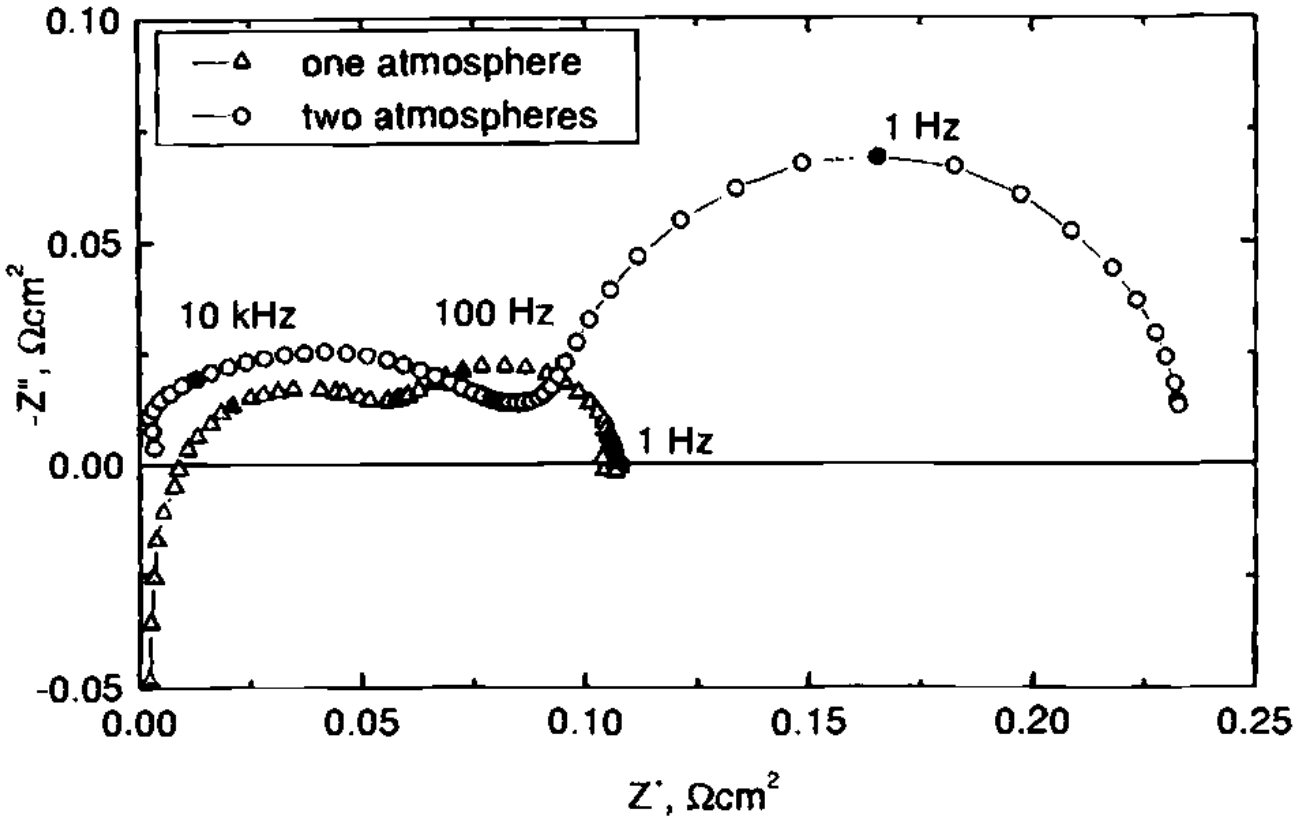


Gas Conversion Impedance

Primdahl and Mogensen. *JES* **145**, 2431 (1998)

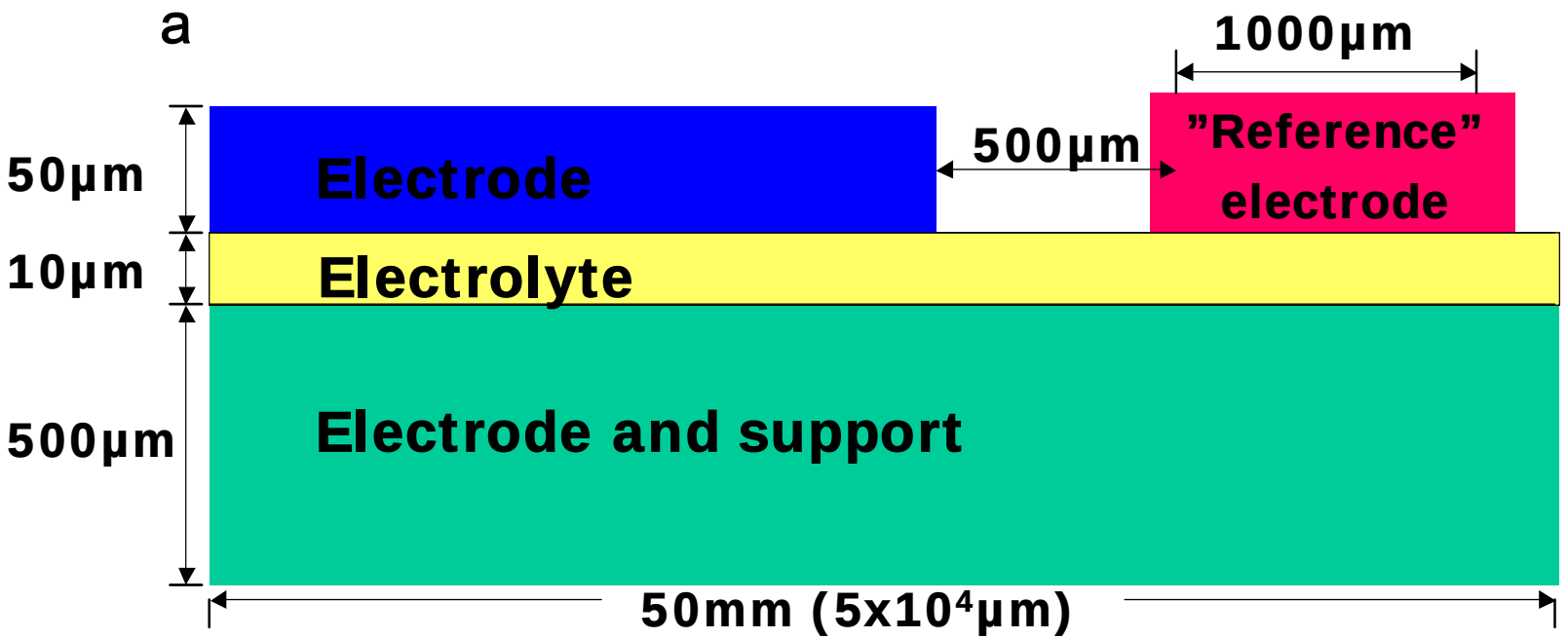
- Given $\Delta x_{H2O} << x_{H2O}$ and $\Delta x_{H2} << x_{H2}$

$$R_g = \frac{RT}{4F^2 J_i}\left(\frac{1}{x_{i,H_2O}} + \frac{1}{x_{i,H_2}}\right)$$

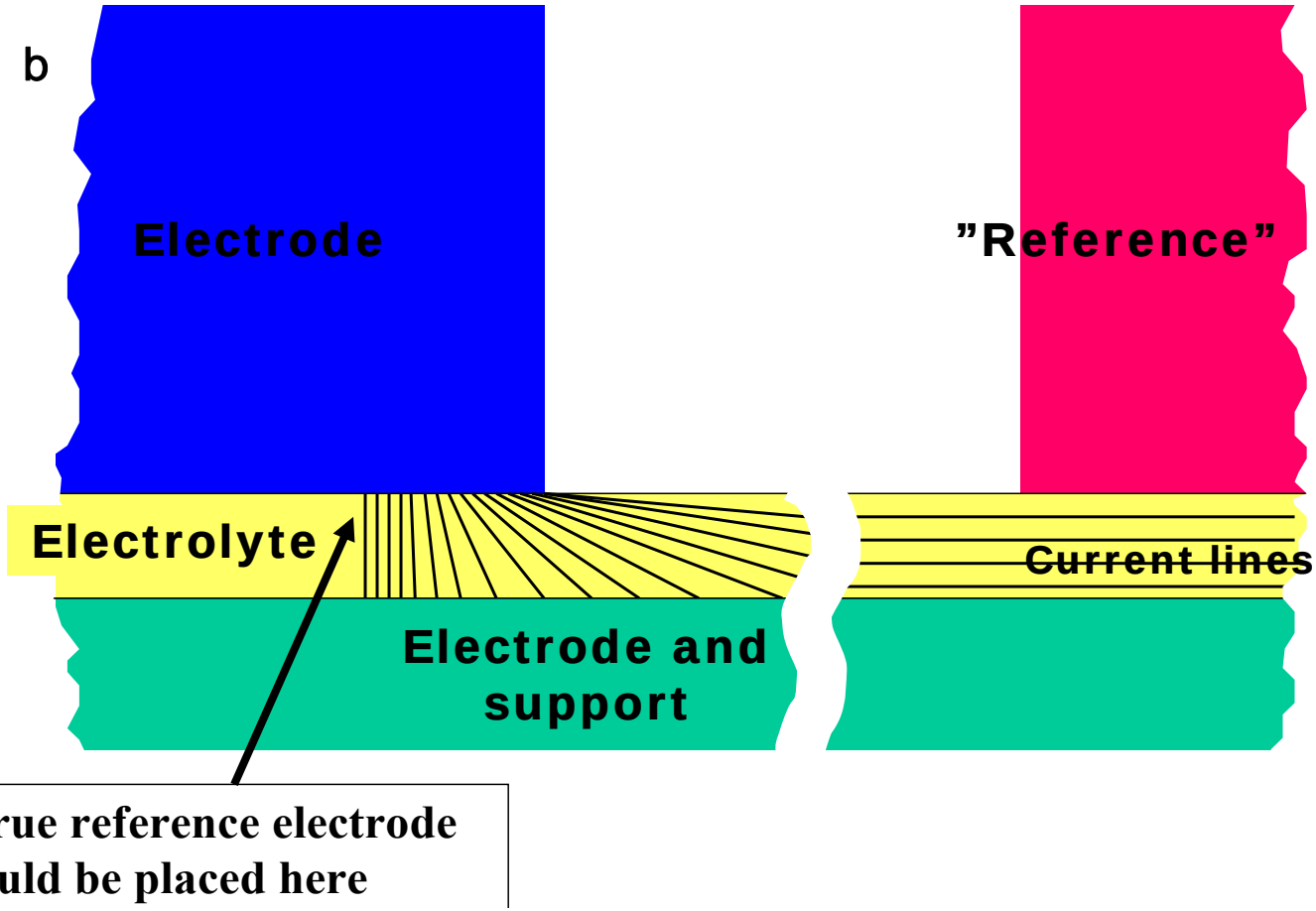
$$C_g = \frac{4F^2 PV}{(RT)^2 A}\frac{1}{\frac{1}{x_{i,H_2O}} + \frac{1}{x_{i,H_2}}}$$

$$f_g = \frac{J_i ART}{2\pi PV}$$

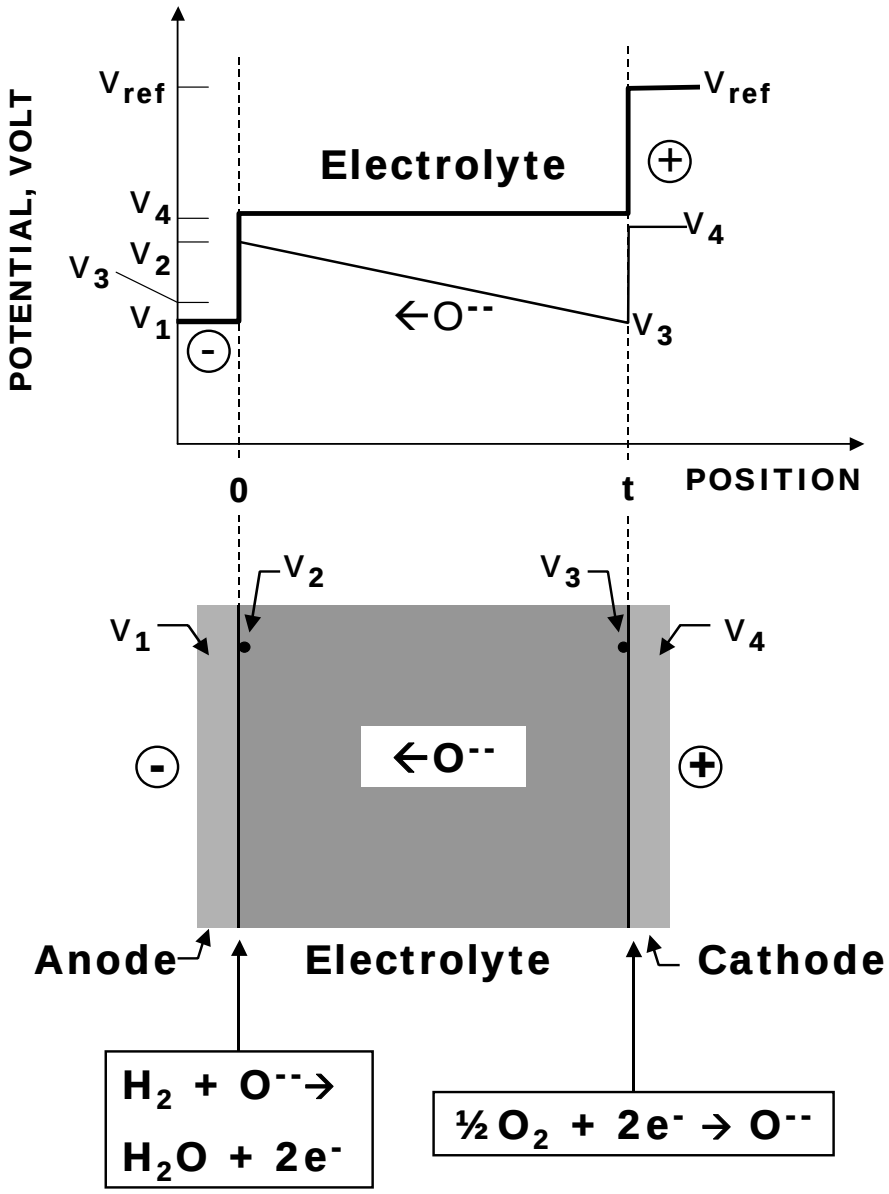
Three electrode set-up problems



This is NOT a three-electrode set-up because the “reference” is not a true reference electrode



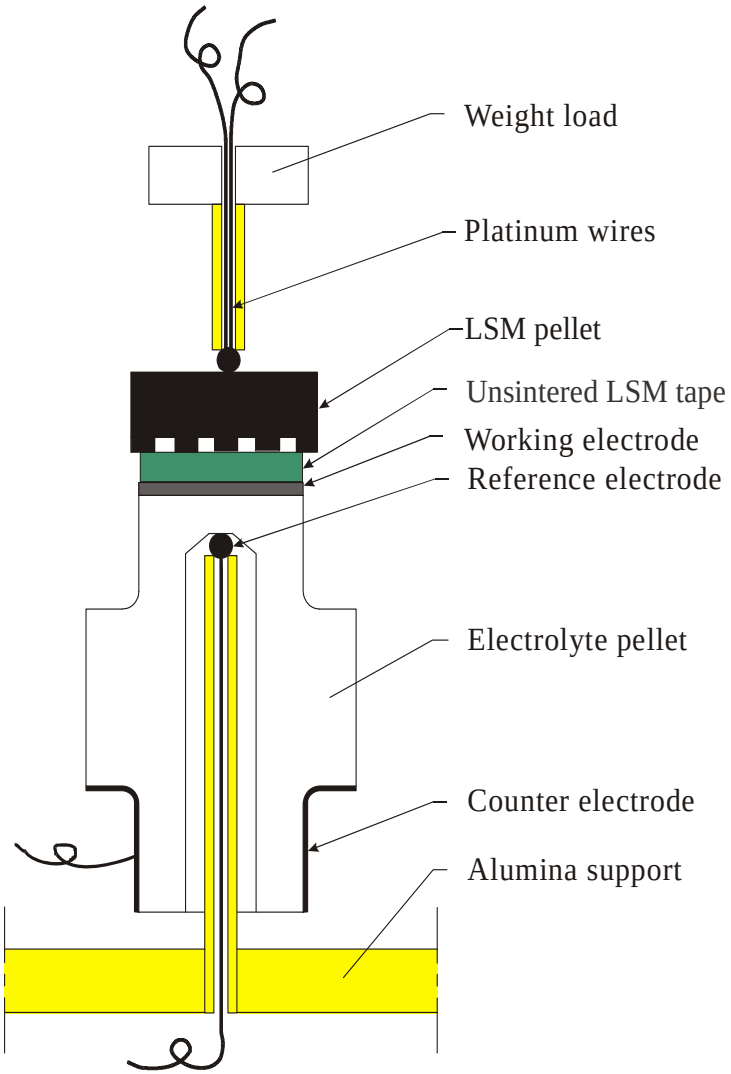
From: Mogensen & Hendriksen, in *High Temperature SOFCs, Fundamentals, Design and Applications*, Eds. Singhal & Kendall, Elsevier 2003, p. 261



The potential across the electrolyte at the "reference" electrode position (thick line) and through the cell part with the current load (thin line).

It is seen that:

$(V_{ref} - V_4)/i = R_{p,anode} + R_{p,cathode} + R_{elyt}$ = the total polarization of the cell apart from concentration polarization.



The Risø 3E-pellet is a proper 3E-set-up, but there are other possibilities

It must be a thick electrolyte, a pellet like thing in case of good electrodes

The Proper Reference Electrode?

By convention it is the standard hydrogen electrode i.e. pH_2 = 1 atm and 25°C

More practical for SOFC studies is an oxygen electrode, pO_2 = 1 atm and the actual temperature

The potential of this may be related to the standard hydrogen electrode potential

Other strategies

- Other methods that may help us to figure out the nature of the rate limitations are to investigate the effect of physical and chemical parameters on the EIS spectra
- Through this we will get information of which kind of processes that the different parts of the EIS relates to.
- Parameters that may give information is apart from temperature and partial pressure of reactant are such as electrode geometry and dimension (thickness), electrode structure isotope composition, gas flow rate, effect of electrode poisons, ...

Electrode mechanisms

- Finally we will have a brief look at what is know and what is proposed about the mechanisms of the hydrogen and the oxygen electrodes of SOC.

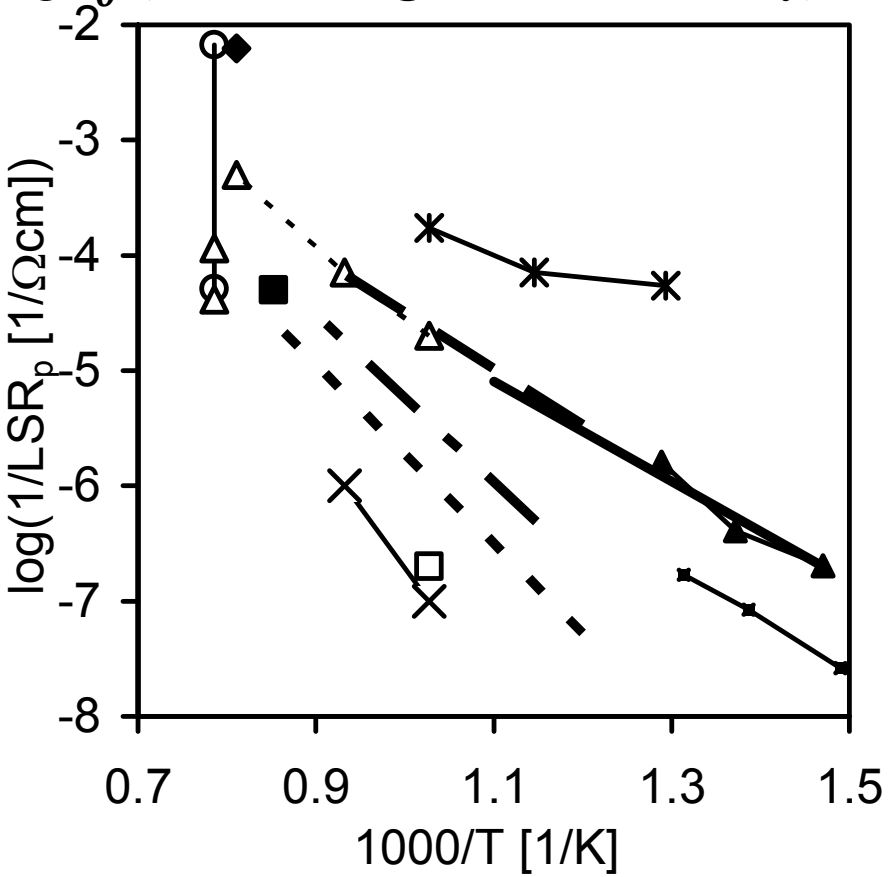
- Even though a lot of data is available, there is still much disagreement about which mechanisms and kinetic expressions that describe the electrode reactions

The TPB ion transfer process $H_2/H_2O/Ni/YSZ$

- Extreme disagreement in the literature
- Activation energies from 0.8 - 1.7 eV!
- Dependencies on partial pressures of water and hydrogen vary a lot - for hydrogen both negative and positive dependencies have been found
- Model electrodes (Ni-point or -pattern) often studied to improve simplicity and reproducibility but with bad luck, see e.g. Mogensen, Jensen, Jørgensen, Primdahl, *Solid State Ionics,* 150 (2002)123-129

Pointed or patterned Ni on YSZ

~ log i_0 (the exchange current density)



Reference		pH_2 [atm]	pH_2O [atm]
Guindet et al.	(29)	0.2	0.0027
Norby et al.	(30)	0.0012	0.006
Mizusaki et al.	(31)	0.01-0.05	0.012-0.0165
Norby	(32)	0.1-1.0	0.0085
Yamamura et al.	(33)	0.01	0.0085
de Boer	(34)	0.905	0.021
Porous modified			
Porous unmodified			
Cermet			
Bieberle	(35)	0.136	0.0005
Vels Jensen		0.97	0.03
Impure	(24)		
Pure	(25)		
Høgh	(38)	0.97	0.03
Up			
Down			
Polarized			

Arrhenius plots for selected results for Ni-SZ electrodes. LSR_p is length specific polarization resistance

Effect of H_2S is dependent on electrolyte type

- A strong effect of the electrolyte composition on the sensitivity to sulfur poisoning has been observed (*K. Sasaki et al., J. Electrochem. Soc., 153, (2006) A2023*):

- While an SOFC with a Ni-YSZ-cermet electrode totally lost its voltage in less than 1 h in a test at 800 °C using H_2 with 20 ppm H_2S as fuel, a Ni-SSZ (scandia stabilized zirconia)-cermet operated stably at almost 600 mV (200 mA/cm2) with 100 ppm H_2S

- This indicates: An important part of the electrochemical reaction takes place at the electrolyte on such Ni-zirconia electrodes

- Also confirmed by Risø DTU. Look for Anke Hagen papers.

H / D isotope effects

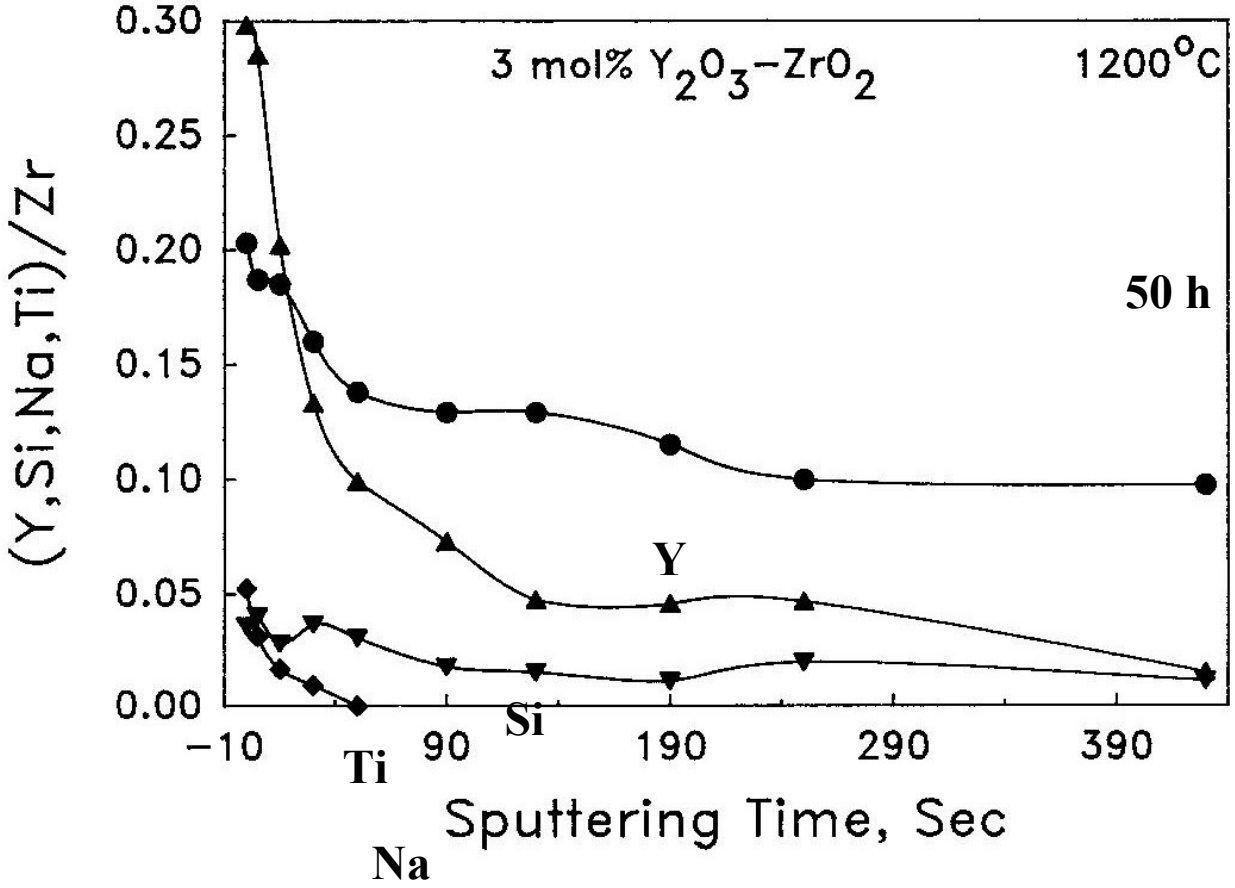
- **For <u>some</u> Ni-zirconia electrodes a clear effect of changing from H_2-H_2O to D_2-D_2O is observed - especially at temperatures below 850 °C - up to a factor of 1.4** (*see e.g. S. Primdahl and M. Mogensen, in SOFC-VI, S.C. Singhal and M. Dokiya, Editors, PV 99-19, p. 530, The Electrochemical Society Proceedings Series, Pennington, NJ, 1999*).

- **This indicates that proton transportation (diffusion or electrical proton conductions) plays an important role in such electrodes**

Dependence on pH_2O

- It seems that the reaction rate (current density) increases with increasing pH_2O in most cases.

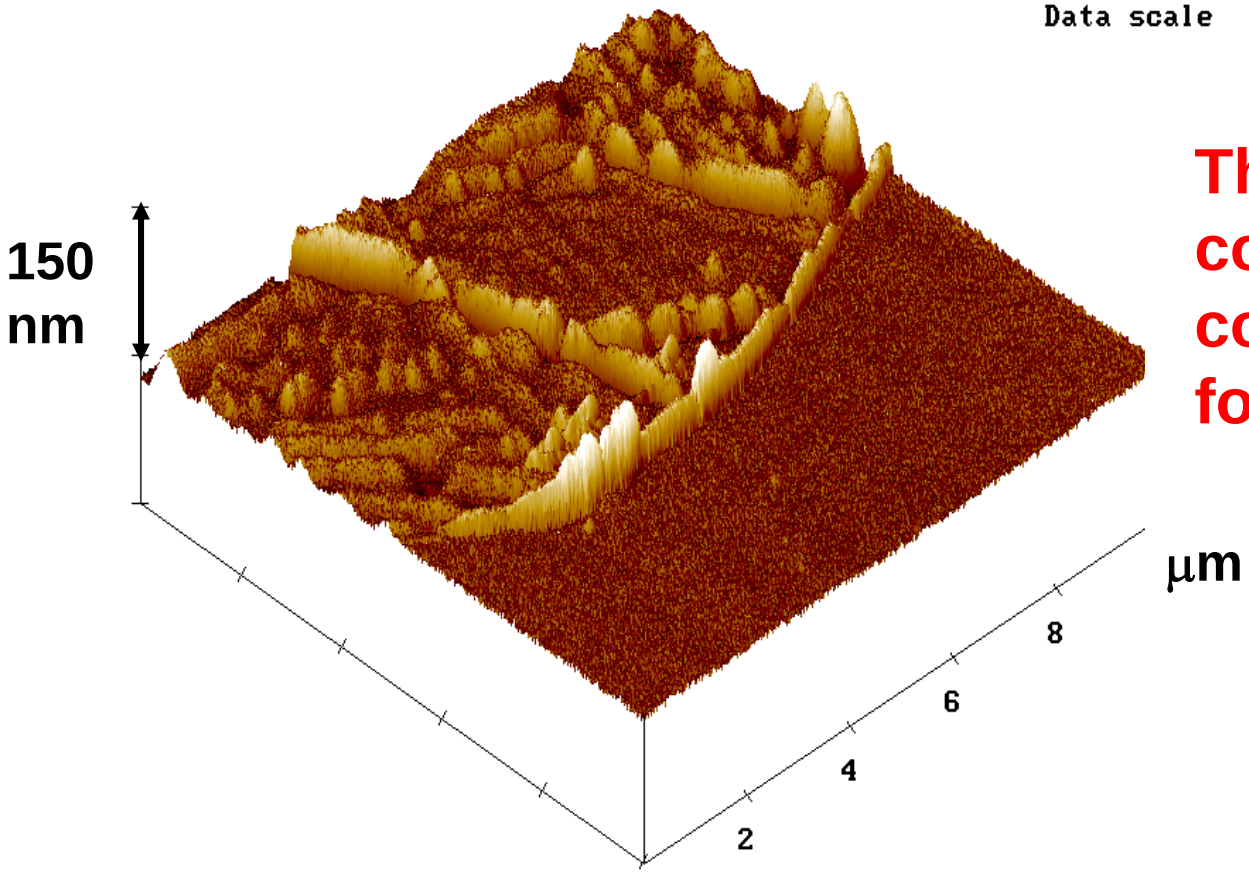
- That the i_0 is dependent is understandable, but it is strange that the anodic oxidation rate of H_2 into H_2O increases with the partial pressure on the reaction product, H_2O.



XPS of YSZ surface. After Badwell and Drennan, 1994.

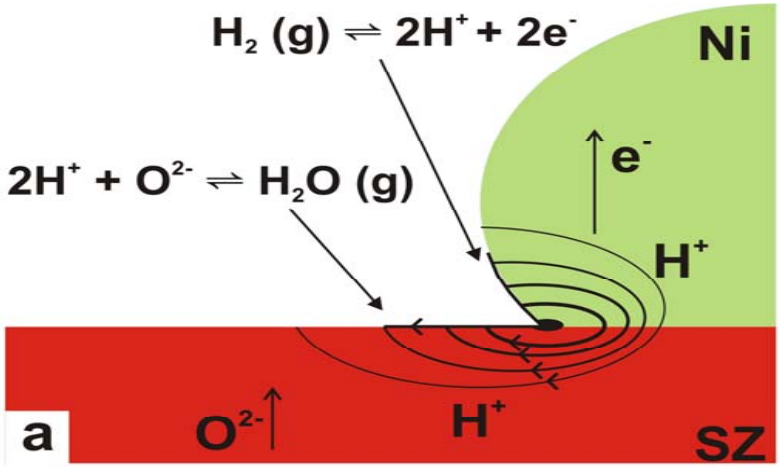
Ni – YSZ Interface

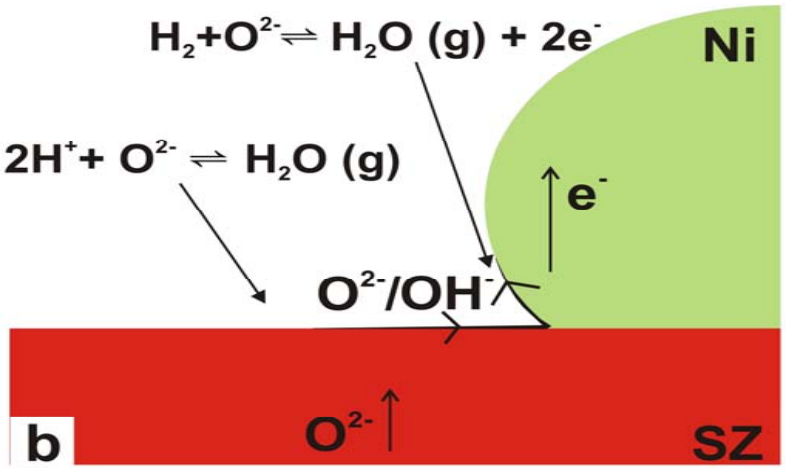
Digital Instruments	NanoScope
Scan size	10.00 µm
Scan rate	1.001 Hz
Number of samples	512
Image Data	Height
Data scale	150.0 nm

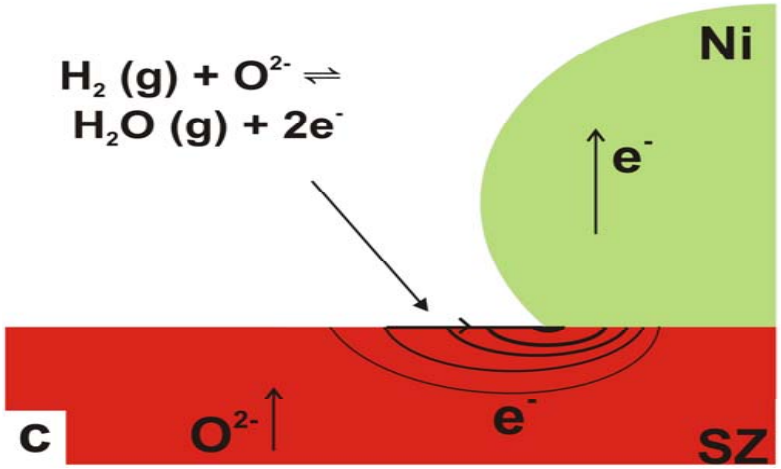


The ”mountains” consist of a non-conducting foreign phase!

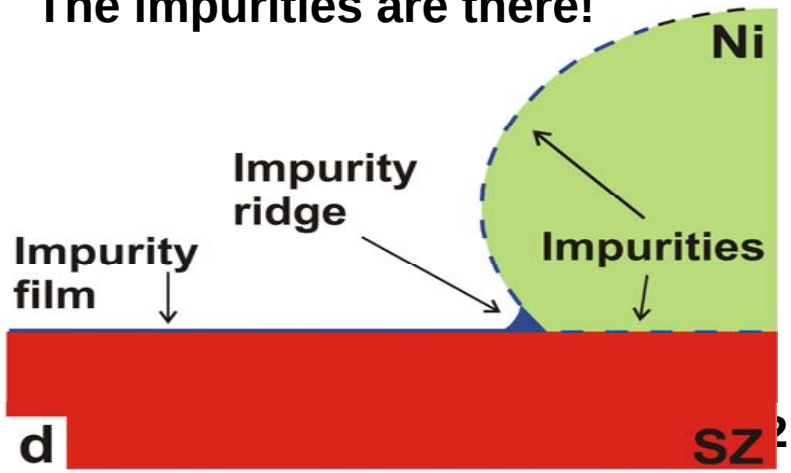
Some possible reaction paths and barriers – but through or around the impurities!







The impurities are there!



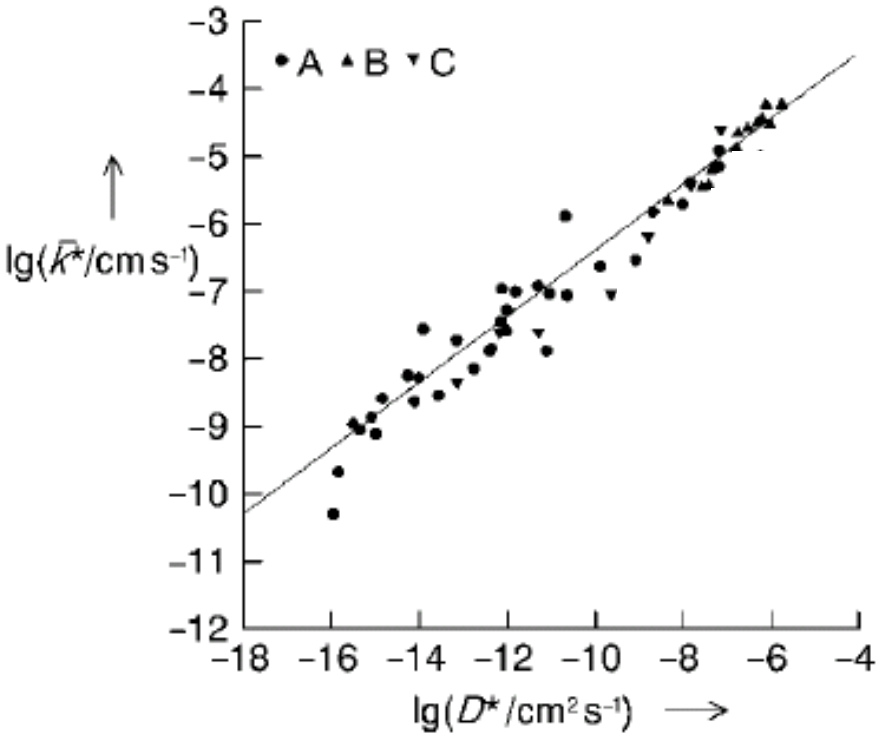
The problem: which $H_2/H_2O/Ni/SZ$ electrode?

- My explanation of the effects of water is that the properties of the segregations at the surface of the SZ and Ni - and in particular at the TPB - changes with P_{H2O} due to up-take or release of water. This will depend on the precise composition of the glassy impurities

- Thus, the problem is: which Ni-SZ-electrode do we have at hand?

- It requires a very tedious and comprehensive characterization of a given electrode before it is possible to give a meaningful detailed mathematical description of the mechanism and the kinetics

Oxygen exchange on ABO_3



Correlation of the effective surface rate constant, k*, with the oxygen tracer bulk diffusion coefficient, D*. A: (La,Sr)(Mn,Co)O3-z, B: (Sm,Sr)(Co)O3-z, C: (La,Sr)(Co,Fe)O3-z for electron-rich transition metal perovskites.

D* is proportional to the vacancy concentration

From R. A. De Souza, J. Kilner, *Solid State Ionics*, **126** (1999) 153 – 161. The proposed relationship logk^* = -1 + 0.5 logD^* (given by the line) is from R. Merckle, J. Maier, H.J.M. Bouwmeester, *Angew. Chem. Int. Ed.*, **43**, (2004) 5069

All measured on single phase bodies/surfaces of the ionic materials using SIMS

Oxygen exchange on ABO_3

R. Merckle, J. Maier, H.J.M. Bouwmeester argue very convincingly that this is consistent with the following reaction:

$\frac{1}{2} O_2 \leftrightarrows O_s' + h\cdot$ fast

$O' + V_O^{\cdot\cdot} \rightarrow O_O^x + h\cdot$ slow oxygen incorporation into ABO_3

A further contribution to the rate limitation is the diffusion of the oxide ions on the surface (or in bulk of the ABO_3)

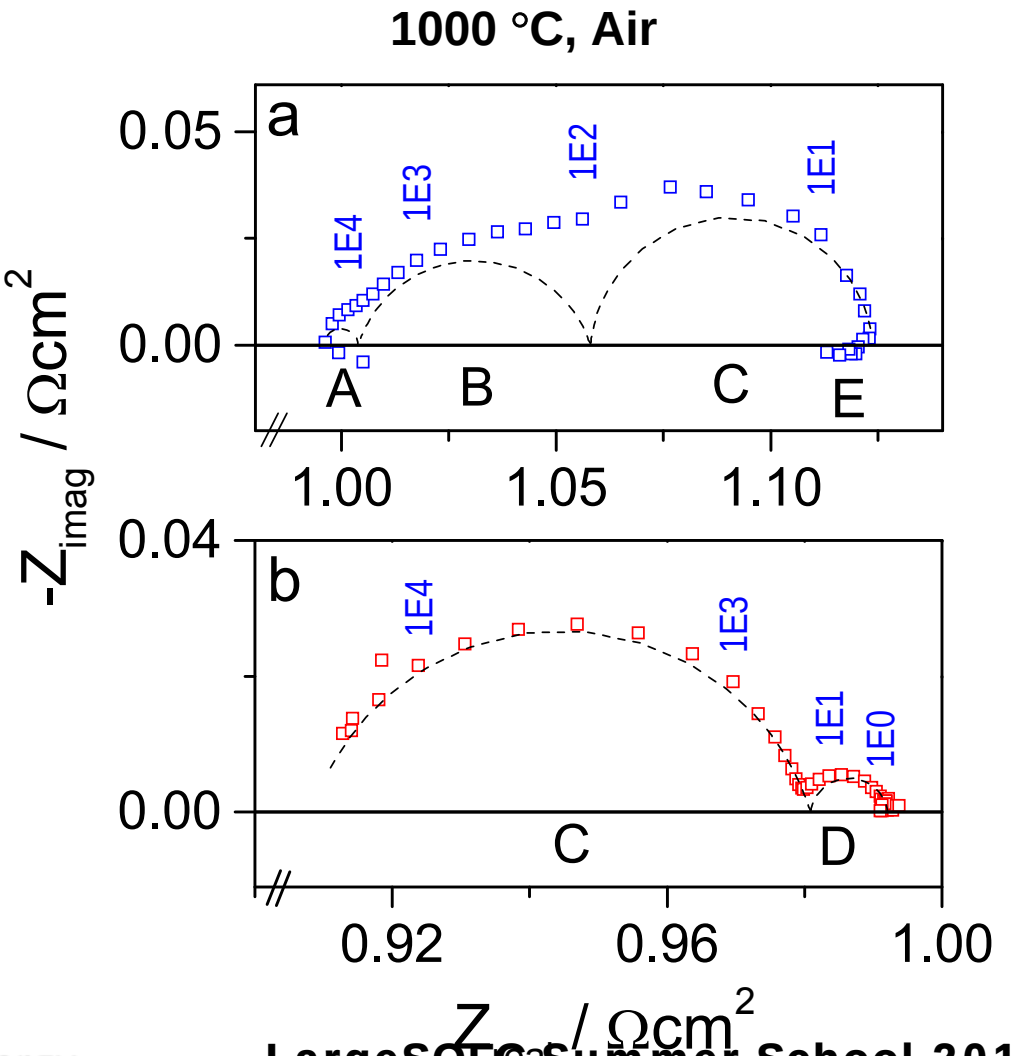
In a real polarized composite electrode even more rate limiting processes are observed

Naturally, the electrode/electrolyte contact area and the three phase boundary (TPB) length are of major importance for the size of the current density

Impedance of LSM/YSZ composite cathodes

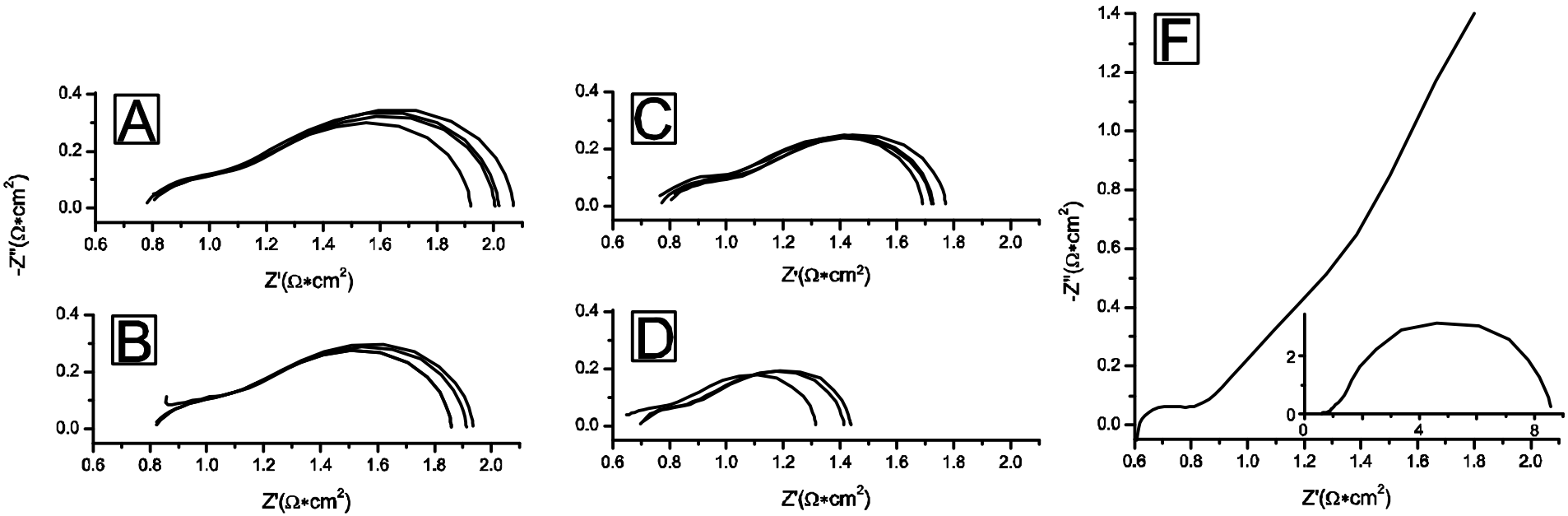
- Spectra may consist of at least five types of arcs
- Arcs A and B is associated with oxide ion transfer through the composite electrode and into the YSZ electrolyte
- Arc C is due to the oxygen incorporation/oxide ion diffusion in/on the ABO_3
- Arc D is caused by O_2 gas diffusion
- Arc E (inductive nature) originates from an activation process

Jørgensen & Mogensen, J. Electrochem. Soc., 148 (2001) A433



EIS of symmetric LSM-YSZ cells

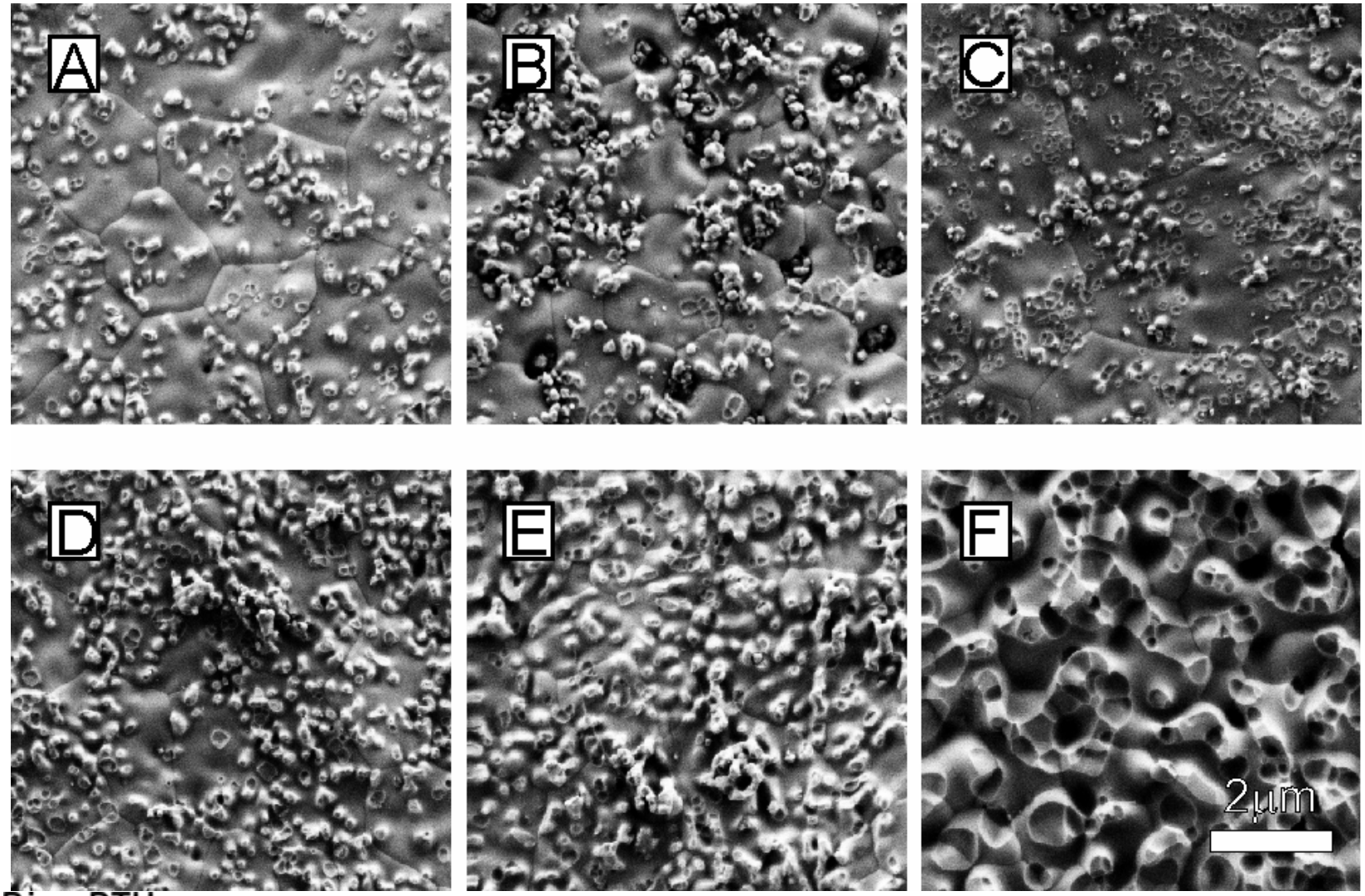
A number of differently prepared electrodes were investigated



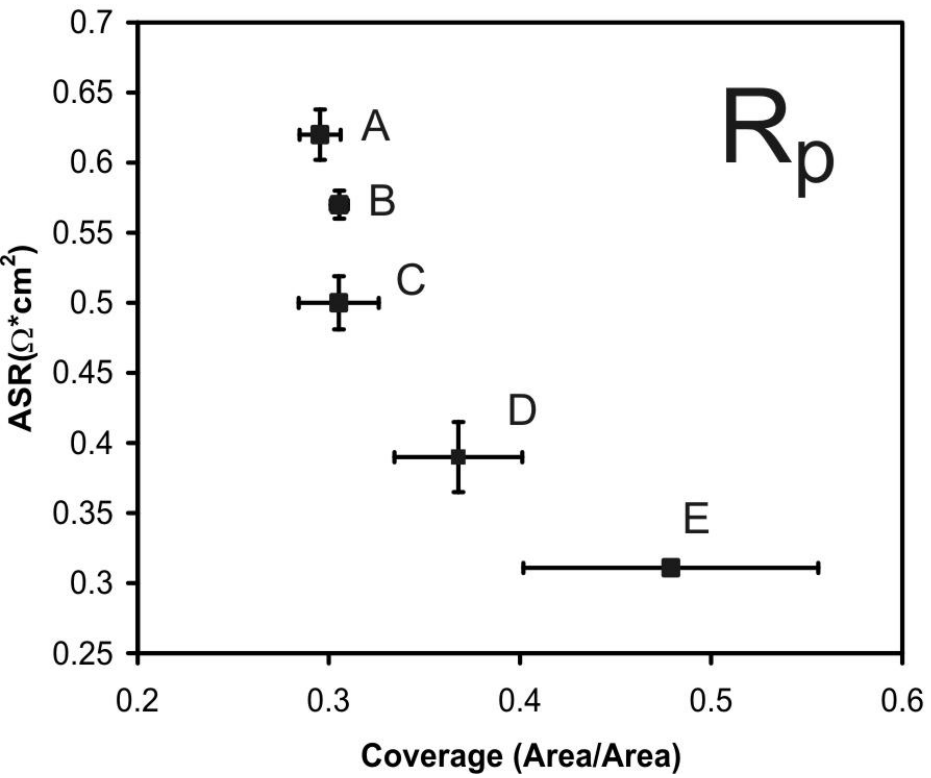
Approx. summit freq. A-D: 0.25 kHz; F: 0.4 Hz (Air, 750 ºC).

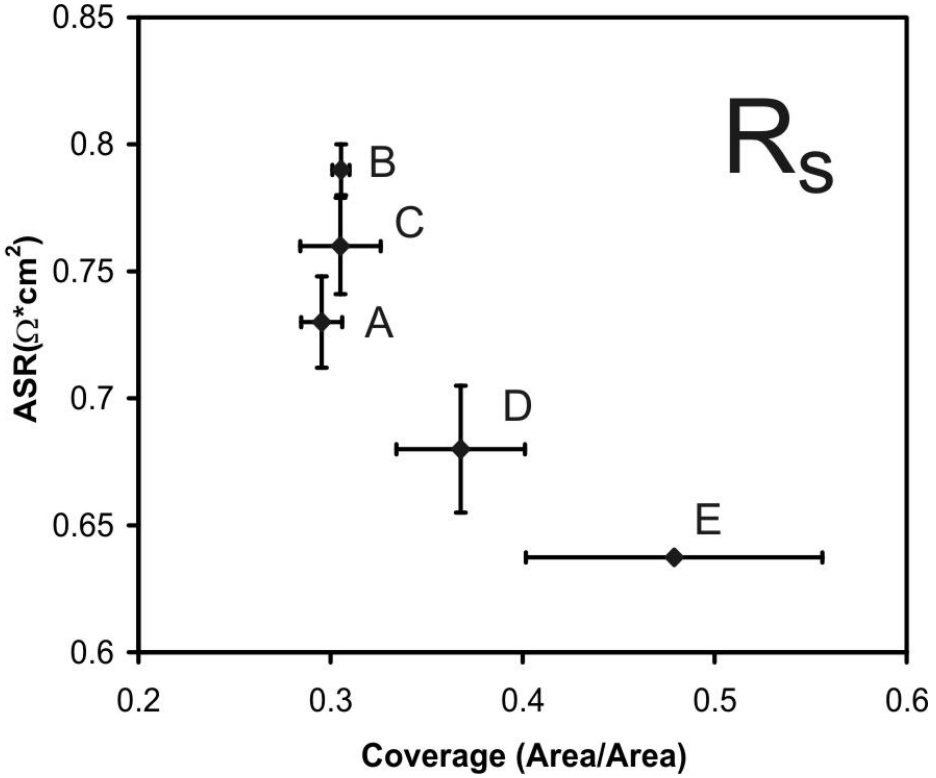
LSM-YSZ / YSZ interface structure

LSM-YSZ electrode removed by acid etching



LSM electrode structure - performance correlation





”Crater area”/total area

Concluding remarks

- **Be aware of the basic theory before starting your experiments.**
- **You have not learned enough during this short lecture!**
- **A lot of literature about SOFC electrode kinetics is rubbish because people have not made proper experiments and interpretations.**
- **So, be critical and do you own better experiments. If you cannot improve then do not.**